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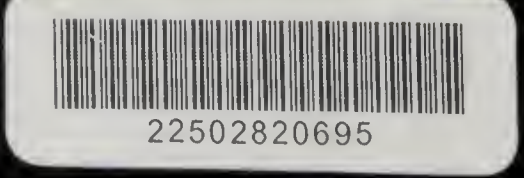
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THE INTERNATIONAL SCIENTIFIC SERIES

EDITED BY F. LEGGE

THE PERIODIC LAW

BY

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PREFACE

So many interesting facts illustrating the periodic variations of the properties of elements when they are considered in the ascending order of their atomic weights have been brought to light during the last few years, that it was thought some attempt should be made to collect the more important and useful of these into one volume.

With such an object in view the present book has been written. In the first half of the book a brief historical account of the efforts made to establish a scientific classification of the elements is given, and this part concludes with the work of Carnelley, who did so much to establish on a firm basis the periodic law as given to the world of science by Mendeléeff. Care has been taken in this part to place before the reader the views held by the proposers of the various schemes, even although more recent investigations may have shown that those views were incorrect. In order that this might be done more effectively reference has been extensively made to the original memoirs, and footnotes are given in all cases to indicate the source from which the information has been obtained.

The more modern applications of the Periodic Law are dealt with in Chapters VII. and IX.

Wherever possible the graphical method of representation has been resorted to, since by such means the facts can be presented in a more concise and striking manner.

The table at the beginning of the book contains the data from which the various diagrams have been prepared, and sections of that table are placed in those parts of the book which deal with particular branches of the subject. A. E. G.

London,
February 1909.

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CHAPTER I

INTRODUCTION—METHODS OF FINDING THE ATOMIC WEIGHTS OF THE ELEMENTS

RESEARCHES in the various branches of Physics and Chemistry are now being carried out so extensively in our own and other countries, and such excellent means for co-ordinating the knowledge obtained from the various sources exist, that it is very difficult to appreciate the manifold difficulties which beset the pioneers in this work during the eighteenth, and the beginning of the nineteenth century.

In the days of its infancy the experiments carried out in Chemistry were almost entirely of a qualitative nature, hence very little progress was made in the classification of the substances experimented with, except in so far as grouping together those which exhibited, or failed to exhibit some well-marked property, such as the power to burn, or not to burn, as the case might be.

Early Ideas.—It is not surprising therefore, that even the phenomenon of combustion should have been explained in a manner quite different from that now accepted. All combustible materials were then supposed to contain a certain something, which conferred

upon them the power to burn. This something was commonly known by the name *Phlogiston*,[1] although it was sometimes spoken of as "a kind of fire material" or "sulphur." This theory held for over one hundred years, although it was known (at least for some portion of that time) that substances increase in weight when burned. This apparent anomaly was explained by assuming that phlogiston possessed a property, "levity," which was assumed to be the converse of gravity, so that, when that substance was expelled by burning the material, an increase in weight must naturally take place.

Lothar Meyer has suggested that this theory may be reconciled with modern ideas if we look upon phlogiston as equivalent to potential energy.

The final overthrow of the phlogiston theory was due to Lavoisier (1743-94). That chemist, by his classical experiments upon the oxidation of mercury, established the fact that the increase in weight which takes place when substances burn in the air, is just counterbalanced by the loss of weight in the air in which the burning takes place.

[1] The idea of phlogiston dates back under various names to the latter part of the fourteenth century (see Radwell, *Phil. Mag.*, 1868). During the greater part of the eighteenth century it was the accepted idea; thus Stahl (1723) looked upon all kinds of matter as built up of phlogiston which was common to all, and a distinguishing substance which conferred those properties which were peculiar to the different types of matter. It is, of course, well known that oxygen when first discovered was known by the name "Dephlogisticated Air," and that Cavendish was an adherent to the phlogistic theory.

Henceforward, combustion was looked upon as due to the oxidation of the combustible material, and this formed the starting-point of experiments along quantitative lines, which led to establishing the law of conservation of matter, a law which has been universally accepted ever since. The researches carried out on the radioactive substances have, however, led Le Bon and others to consider the advisability of modifying this belief.

Another important result which was brought about by the introduction of quantitative methods, was the arrangement of substances into elements and compounds.

The idea of elements, or elementary substances, was of course by no means a new one, for the early philosophers of Greece adopted a system, in which they supposed the material universe to be made up of four so-called elements, viz. :—earth, air, fire, and water. To these, Aristotle added a fifth, which he assumed to be non-material in nature, and which occupied all space. This became known as the quintessence.

Each of the four elements was supposed to possess two properties selected from warm and cold, moist and dry. Thus, the earth was cold and dry, the air warm and moist, fire warm and dry, and water cold and moist.[1]

[1] The history of chemistry reveals the fact that many other ideas respecting elementary substances were held at various times. Thus Robt. Boyle, (1627-91) in his "Sceptical Chemist," tried to upset the salt, sulphur, and mercury theory of the Alchemists, as well as the ideas on the subject as taught by Aristotle. In the same work he gave a scientific definition of an element. How mixed up the

The system of elements introduced as the outcome of quantitative experiments was, however, quite distinct from this, being in fact, the same as that recognized at the present day.

The earlier investigations of the proportions by weight and volume in which elements combine, were largely the works of Richter, (1762-1807) and, (more particularly so), of Proust (1754-1826). To the latter chemist is due the distinction of having pointed out the distinctive mark of a chemical compound, for he stated most emphatically, that all chemical compounds contain their constituents in fixed and invariable proportions. Richter also had stated that all true chemical changes take place between definite weights or volumes of the substances concerned. During the years 1811-12 Berzelius confirmed these observations, and carried out much more extended quantitative researches, yet, as will appear in the sequel, a great many years elapsed before any successful attempt at a classification, to embrace the whole of the elements, was made.

During the early part of the nineteenth century, Dalton worked at, and formulated, his Atomic Theory.

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whole subject became is well illustrated by the following passage from "On the Elementary Principles of Nature," by Edward Peart, M.D., 1789, p. 24. "The elementary principles of nature, therefore, are three, two active, and one more passive or fixed. The two active principles are Æther and Phlogiston; and each of these, by their union with the more passive principles, forms a secondary or more fixed principle; a fixed particle of matter, with an æthereal atmosphere forms an earthly particle or principle; and with a phlogistic atmosphere, the acidifying principle."

He is often spoken of as the founder of that theory, and to a very large extent this is true. The idea that all substances are built up by the union of particles which are themselves indivisible, dates back to a much earlier period, yet, as has been stated, the experiments carried out prior to the beginning of the nineteenth century were of such a nature, that the systems of chemistry based upon them, dealt with the subject from a qualitative standpoint only. Dalton, on the other hand, introduced quantitative considerations into his chemical work, and in this, his work on the atomic theory is distinguished from that of all his predecessors.

He considered the atom to be the smallest particle which could enter into composition with other particles to form a chemical compound, and also that the atom itself was indivisible. In his " New System of Chemical Philosophy," published in 1808, he recognized the indestructibility of matter as an established fact, and also states specifically the problem he hoped to be able to solve by the aid of his atomic theory. It was, to obtain the relative weights of the ultimate particles of both simple and compound bodies, and the number of constituent ultimate particles in each compound particle. In the latter connection he was led into the grave error of assuming, that if only one compound of two substances existed, the ultimate compound particle consisted necessarily of only one atom of each of the constituents.

On this account, many of the relative atomic weights

obtained by him were quite different from those now accepted. Thus, Dalton looked upon ammonia as a compound formed by the union of one atom of nitrogen with one atom of hydrogen, and, as he found in this case that 4·7 parts by weight of nitrogen united with one part by weight of hydrogen, he considered the atomic weight of nitrogen to be 4·7 ; whereas, we now know that in ammonia three volumes of hydrogen have united with one of nitrogen, so that the atomic weight of nitrogen must be just three times that accepted by Dalton.

In these early experiments on the relative atomic weights, the various chemists were by no means of one accord as to the standard of comparison which should be adopted.

Dalton proposed the atom of hydrogen as unity, since that element was known to be the lightest of all the elements, while Wollaston and Berzelius both proposed that oxygen should be adopted as the standard. Even then, Wollaston referred to oxygen as having a value 10, and Berzelius referred to it as equivalent to 100. Such a state of affairs was necessarily detrimental to the discovery of any general classification of the elements based upon the relationships which exist between their atomic weights.

Methods of determining Atomic Weights.—As the correct determination of the relative atomic weights of the elements is essential before any relationships between the elements depending on their atomic weights can be

established, a brief consideration of the methods employed in obtaining the atomic weights of the elements will not be out of place.

Shortly after Dalton had brought forward his atomic theory, Gay Lussac formulated a law with respect to the combination of gases by volume, which may be stated as follows. When gaseous substances combine, they do so in simple ratios by volume, so that, if the volume of one of the constituents is represented by unity, that of the other will be represented by one, two, or at the most three, and the volume of the compound substance formed, is also simply related to the volume of one of the constituents. Thus, one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrochloric acid; two volumes of hydrogen unite with one volume of oxygen to form two volumes of water vapour; and one volume of nitrogen combines with three volumes of hydrogen to form two volumes of ammonia.

Now, if two volumes of water vapour contain two volumes of hydrogen and one volume of oxygen, it is quite clear that one volume (the ultimate particle of Dalton) of water vapour, will contain one volume of hydrogen and only half a volume of oxygen. This would mean that the atom of oxygen was capable of splitting into two portions, and that quantities of smaller dimensions than an atom were capable of entering into combination with other substances to form chemical compounds. This, according to Dalton's theory, was an impossibility, and so it became necessary to reconcile

these apparently conflicting statements. Then it was that Avogadro introduced the idea of "a molecule," as the simplest portion of a compound, and at the same time arrived at the conclusion, that equal volumes of gases under the same conditions of temperature and pressure, contain the same number of molecules.

Vapour Density Method.—If the truth of Avogadro's statement is accepted, it becomes at once apparent, that, although it may not be possible to compare the individual molecules of two gases, yet, if the weights of equal volumes of two gases are found under precisely similar conditions, the ratio of their molecular weights can be at once obtained, by comparing the weights of the gases so found.

Thus, if we know the weight of a litre of hydrogen gas at 0° C., and at a pressure of 760 mm. of mercury, and also the weight of a litre of nitrogen under the same conditions, we have at once the molecular weight of nitrogen in terms of that of hydrogen.

If we assume the molecular weight of hydrogen to be represented by 2, then the molecular weight of nitrogen will of course be

$$\frac{\text{Weight of a litre of nitrogen at 0° C. and 760 mm. pressure}}{\text{Weight of a litre of hydrogen at 0° C. and 760 mm. pressure}} \times 2.$$

From this alone, it would be quite impossible to state the atomic weight of nitrogen in terms of hydrogen as unity. It is first necessary to know how many atoms of nitrogen are contained in its molecule. The following examples will help to make this point clearer. The

moleeular weight of nitrogen as found by the above method is 28·02, and from other eonsiderations we know that its moleeule eontains two atoms, so the atomie weight is 14·01. The moleeular weight of mereury is 199·8, but its atom is also its moleeule, henee its atomie weight is 199·8; on the other hand, the moleeular weight of phosphorus is 123·84, while its atomie weight is only 30·96, indicating that its molecule eontains four atoms. Thus the moleeules of all the elements do not eontain the same number of atoms, and, in fact, it is not possible to give a definite rule on this matter to include all the elements. Generally speaking however, the non-metallie elements, and those whieh possess a semi-metallie nature, have moleeules containing two or more atoms, while the moleeules of the true metals are monatomie.

In order to decide what number shall be used to indieate the atomie weight, or in other words, to aseertain whether the number obtained for the molecular weight is also the atomic weight, or some multiple of it, it is neeessary to analyse as many gaseous compounds whieh eontain the substanee, as is possible, so as to find out the proportions by weight in whieh it oeeurs with respect to the other elements present.

The moleeular weights of all these gaseous compounds must be observed, and then the exact amount of the element whieh is contained in the molecular weight of each of the compounds, calculated. The smallest number so obtained, of eourse represents the smallest quantity whieh is known to enter into combination with

other substances, and is therefore accepted as the atomic weight.

As an example of this method, suppose it is required to find the atomic weight of oxygen, and the gases, SO_2, CO_2, and N_2O are used. [It is to be understood that all the gaseous compounds containing the element should be examined, but these will be sufficient to illustrate the method.]

When equal volumes of these gases and of hydrogen are weighed under precisely similar conditions of temperature and pressure, let the weights found for SO_2, CO_2, N_2O, and hydrogen, be in the proportion 64 : 44 : 44 : 2.

Then, by analysis and synthesis of SO_2, it is found that 50 per cent. of its weight consists of oxygen. Similarly, it is found that 72·7 per cent. of the weight of CO_2 is oxygen, and 36·3 per cent. of N_2O by weight is also oxygen.

Now 50 per cent. of 64 is 32, and
72·7 per cent. of 44 is also 32, while
36·3 per cent. of 44 is 16 nearly.

16 being the smallest number so obtained, is then taken as the atomic weight of oxygen.

Many difficulties however stand in the way of determining the atomic weights of the elements from their vapour densities. The gases must be of a homogeneous nature, or errors will most surely occur. It was due to an error of this description that the presence in

the atmosphere of the inert gases of the argon type became known. The atomic weight of a specimen of nitrogen which had been prepared from the air, was found to be slightly different from that of nitrogen prepared from other sources, even when the greatest precautions were taken to avoid error. Rayleigh and Ramsay found that this was due to the fact, that small quantities of argon were mixed with the atmospheric nitrogen. Again, some substances such as ammonium chloride, etc., when heated undergo dissociation, while in the case of certain compounds such as those of aluminium, the vapour densities obtained are too high if the observations are carried out at too low a temperature. The compounds of the metals also do not as a rule exist in the gaseous state under ordinary conditions, so that other methods of determining the atomic weight must be used in such cases.

Atomic Heat.—In 1819 Dulong and Petit published an account of their researches with respect to the connection between the atomic weights of the elements and their specific heats. [By the specific heat of a substance, is meant the amount of heat required to raise the temperature of one gram of that substance 1° C., as compared with the amount necessary to raise the temperature of one gram of water from 0° C. to 1° C.]

They came to the conclusion that the specific heats of the elements are roughly inversely proportional to their atomic weights, that is, the product of the atomic

weight by the specific heat is a constant for all elements which are solid at ordinary temperatures and pressures. The term atomic heat is often used to indicate this constant.

This law must be looked upon as only approximately true, since it has now been found that the specific heat, and consequently the atomic heat, depends to some extent upon the range of temperature, and also the absolute temperature, for which it is determined. Yet it has served a very useful purpose, for by its help it has often been found possible to pick out the most probable value for the atomic weight of an element, from a number of possible values.

Speaking very generally it may be assumed that the atomic heat of the metals has an average value 6·4. Thus iron has atomic weight 55·9, specific heat 0·116, and therefore atomic heat $55{\cdot}9 \times 0{\cdot}116 = 6{\cdot}48$ about. To show how this law may be applied to determine the true value of the atomic weight of some element, let us consider the following well-known examples.

Sir William Crookes discovered the element thallium by means of the spectroscope, and it was subsequently found that thallium is closely allied to both lead and the alkali metals, so far as its characteristic properties are concerned. If it is classed with lead, the atomic weight of thallium, obtained by considering its chloride as similar in composition to lead chloride, would have to be 407·2. When thallium is classed with the alkalies so that one atom of thallium is united with only one

atom of chlorine to form the chloride, its atomic weight becomes 203·6.

Regnault found the specific heat of thallium to be 0·0335, and this quantity when multiplied by 203·6, gives as a product 6·8, which at once settles the question of atomic weight in favour of 203·6. Again, the elements cerium, and lanthanum, were for a long time considered as dyads, their lowest oxides being supposed to be represented by the formulæ CeO, and LaO. If this were the case then their atomic weights must be: cerium 94·1, and lanthanum 92·7. Bunsen found on the other hand, that their specific heats were: cerium 0·04479, and lanthanum 0·04485. Now, $0{\cdot}04479 \times 94{\cdot}1 = 4{\cdot}2$ about, and this quantity would therefore represent the atomic heat of cerium if its atomic weight was 94·1.

If, however, these elements are considered as triads, and their oxides have a composition of the type R_2O_3, the atomic weights then become: cerium 141·2, and lanthanum 139·0, and their atomic heats, 6·3 and 6·2 respectively; thus bringing them into line with the other elements, so far as Dulong and Petit's law is concerned.

For a long time it was an extremely doubtful question as to whether the atomic weight of beryllium was 9·2, 4·6, or 13·8. The matter was eventually settled by Emerson Reynolds,[1] who obtained his result by showing that 9 centigrams of beryllium, and 108 centigrams of silver, if both were heated to 100° C., gave out equal quantities of heat in cooling through the same range of

[1] *Phil. Mag.* [5] 3, 1877, pp. 38-42.

temperature. Since 108 is the atomic weight of silver, it is quite clear that the atomic weight of beryllium cannot be a multiple or submultiple of 9, if Dulong and Petit's law is to hold good in this case.

Newmann and Kopp extended the application of this law, by proving that the atomic heat of elements remained the same even when those elements were in combination with other elements. As this is the case, it becomes possible to deduce the atomic heats of some elements such as oxygen, hydrogen, etc., from the molecular heat of the compounds containing them. The molecular heat of mercuric oxide for instance, has been found by experiment to be 10·4, then the atomic heat of mercury being 6·4, that of oxygen is 4.

Yet, it is perhaps much better to restrict this law to the consideration of solids, and even for these the results are by no means constant, as can be seen from the accompanying table.

Tilden, in 1900 [1] found that even in the cases of the most closely allied metals, such as nickel and cobalt, the atomic heats are not exactly the same, that of cobalt being 6·03,[2] and nickel 6·31.[2] He also calculated the atomic weight of platinum from that of gold, on the assumption that their atomic heats were the same. The result he obtained by this method was 188·8 [2] instead of 193·41,[2] again showing that Dulong and Petit's law must be regarded as an approximation only.

[1] *Phil. Trans.* 194, p. 240.

[2] Figures as given by Tilden, p. 240.

The specific heat of a metal is affected by a variety of circumstances, of which, perhaps, its mechanical condition is the most important. Thus Regnault found the specific heat of hammered copper to be 0·0935, and of annealed copper, 0·0952. According to Tilden's results, porous unfused metals all give values for the specific heat which are slightly lower than those obtained after fusion.

It has for a long time been known, that the specific heat depends upon the temperature, and Tilden thought, from his experiments on nickel and cobalt, the atomic heats of which approached the common value 4, at very low temperatures, that after all it might be proved that the specific heats of all the metals were inversely proportional to their atomic weights at a certain definite temperature. Subsequent experiments carried out by him on silver, did not fulfil his hopes in this respect.

Several elements, in particular carbon, boron, and silicon, have atomic heats which diverge very considerably from the average value 6·4. Weber[1] investigated the atomic heats of these elements, and found that the variation with temperature was very large, as is shown in the following table :—

Carbon as Diamond.		Carbon as Graphite.		Crystallised Silicon.		Crystallised Boron.	
Temperature.	Atomic Heat.	Temperature.	Atomic Heat.	Temperature.	Atomic Heat.	Temperature.	Atomic Heat.
−50·5° C.	0·762	−50·3° C.	1·3656	−39·8° C.	3·880	−39·6° C.	2·1065
986·8° C.	5·5464	981·6° C.	5·6256	232·4° C.	5·6812	600° C.	5·5

[1] *Phil. Mag.* [4] 49. pp. 161, 276.

TABLE OF ATOMIC HEATS

Atomic weights as given in 1908 *list*

Element.	Atomic Weight Oxygen = 16	Specific Heat.	Atomic Heat.	Remarks.
Lithium	7·03	0·94	6·6	
Beryllium	9·1	0·506	5·01	Sp. Heat 0° to 300° C.
Boron	11·0	0·366	4·02	Specific Heat of Crystalline Boron at 233° C.
Carbon	12·0	0·459	5·50	Sp. Heat of diamond at 985° C.
Sodium	23·05	0·293	6·74	
Magnesium	24·36	0·25	6·09	
Aluminium	27·1	0·24	6·5	Sp. Heat at 300° C.
Silicon	28·4	0·203	5·73	Crystalline at 232° C.
Phosphorus	31·0	0·20	6·2	Yellow.
Sulphur	32·06	0·234	6·5	Sp. Heat 119° to 147° C.
Potassium	39·15	0·166	6·5	
Calcium	40·10	0·153	6·28	Sp. Heat 0° to 157° C.
Scandium	44·1	0·152	6·7	Sp. Heat 0° to 157° C.
Titanium	48·1	0·129	6·2	Sp. Heat 0° to 211° C.
Vanadium	51·2	0·115	5·89	
Chromium	52·1	0·112	5·83	Sp. Heat at 100° C.
Manganese	55·0	0·121	6·65	
Iron	55·9	0·116	6·48	
Cobalt	59·0	0·107	6·31	
Nickel	58·7	0·11	6·45	
Copper	63·6	0·098	6·23	Sp. Heat at 300° C.
Zinc	65·4	0·095	6·21	

Gallium	70·0	0·0802	5·6	Liquid.
		0·079	5·5	Solid.
Germanium	72·5	0·0773	5·6	Sp. Heat 0° to 211° C.
Arsenic	75·0	0·083	6·22	Crystalline.
Selenium	79·2	0·084	6·65	Crystalline.
Bromine	79·96	0·084	6·74	Solid Sp. Heat – 79° to – 20° C.
Zirconium	90·06	0·066	5·98	
Molybdenum	96·0	0·0659	6·32	
Ruthenium	101·7	0·0611	6·21	
Rhodium	103·0	0·058	5·97	
Palladium	106·5	0·059	6·28	
Silver	107·93	0·0568	6·13	
Cadmium	112·4	0·061	6·84	Sp. Heat at 300° C.
Indium	115	0·057	6·55	
Tin	119	0·055	6·54	
Antimony	120·2	0·0536	6·44	Sp. Heat at 300° C.
Tellurium	127·6	0·05	6·38	
Iodine	126·97	0·054	6·85	
Cæsium	132·9	0·048	6·38	
Lanthanum	138·9	0·0448	6·22	
Cerium	140·25	0·0448	6·28	
Tantalum	181	0·033	5·97	
Tungsten	184	0·035	6·44	
Osmium	191	0·0311	5·94	
Iridium	193	0·0323	6·23	
Platinum	194·8	0·0324	6·3	At 1600° Sp. Heat of platinum is 0·0398.
Gold	197·2	0·0324	6·4	
Mercury	200·0	0·0333	6·66	
Thallium	204·1	0·033	6·73	
Lead	206·9	0·0315	6·51	
Bismuth	208·0	0·0303	6·30	
Thorium	232·5	0·0275	6·39	
Uranium	238·5	0·028	6·67	

He concluded from his experiments that the atomic heat of these elements becomes constant on reaching a certain temperature ; in the case of carbon and boron, this temperature is about 600° C., and for silicon about 200° C.

Of course it is quite possible that some of the discrepancies which exist in the accepted atomic heats may be due to the difficulty of obtaining the element in an absolutely pure form, or even, in some cases, to oxidation taking place during the course of the experiment ; and it may ultimately be shown that closely allied elements other than nickel and cobalt, may have exactly the same atomic heats at some particular temperature. Be this as it may, the law has fulfilled a very useful purpose as a sort of filter for the atomic weights.

Electro-Chemical Equivalents.—If an electric current is sent through some water made conducting by the addition of a few drops of sulphuric acid, and also through a solution of silver nitrate, and the quantity of hydrogen liberated in the one, and the increase in weight of the negative electrode due to the deposition of silver in the other, be noted, it will be found that when one milligram of hydrogen has been collected 108 milligrams of silver will have been deposited. For this reason 108 is looked upon as the electro-chemical equivalent of silver.[1] Faraday was the first to notice

[1] The electro-chemical Equivalents of the elements are usually stated in grammes per coulomb, or that quantity multiplied by some constant such as by 1000. Thus that of silver in grammes per coulomb × 1000 = 1·1180.

results of this kind, and the law which states, that "if one and the same current is passed through two electrolytes, the elements deposited are chemically and electrically equivalent to one another," is due to him.

It sometimes happens that more than one electrochemical equivalent is obtained for the same element when experimenting with different compounds. As an example of this, solutions of ferrous and ferric chlorides could be taken. With the ferrous chloride the equivalent of the iron would be found to be $\frac{56}{2} = 28$, while with the ferric compound it would be $\frac{56}{3} = 18{\cdot}6$.

Again, all compounds are not conductors of electricity, and so cannot be decomposed in this way.

Some elements, like silver, are able to take the place of one atom only of hydrogen when they form salts by neutralisation of acids; thus HCl, AgCl; and HNO_3, $AgNO_3$.

Others are able to replace two or more atoms of hydrogen; thus $2Fe + 6HCl = Fe_2Cl_6 + 3H_2$.

The ability of an element to act in this manner constitutes what is known as its *Valency*. The term *Equivalent* is therefore used to denote that quantity of an element which can enter into combination with one part by weight of hydrogen, or can replace that quantity in a compound, because, if we exclude the argon group, which appears to have no valency at all, no element has a lower valency than hydrogen; that is, no compound can be formed by the union of one atom of hydrogen with more than one atom of a second element.

If we consider this in relation to Faraday's law, the connection between valency and equivalent will be still more apparent. The current which liberates the atomic weight of silver from one of its compounds is also able to liberate the atomic weight of hydrogen from water, so that silver has the same valency as hydrogen, and is consequently known as a monad. On the other hand, the same current would liberate from the solution of a copper salt only one-half the atomic weight of copper. This quantity is known as the equivalent of the copper, and it is quite clear that when the atomic weight of copper has been liberated, twice the atomic weight of hydrogen will have been collected. Hence, one of copper can replace two of hydrogen, and copper therefore is said to be a dyad.

Other elements such as boron, phosphorus, etc., are triads; while carbon, silicon, sulphur, etc., are tetrads.

We may represent this by saying that Valency × Equivalent = atomic weight.

As hydrogen is taken as the standard of reference in this respect, the quantivalence of any element which forms a stable volatile compound with hydrogen could be at once ascertained, since the number of hydrogen atoms united with one atom of the other element would represent its valency. Only a relatively small number of elements, however, form such compounds. Many metals, on the other hand, unite with the monad organic radicals such as methyl (CH_3), and these can be considered as taking the place of hydrogen,

e.g., $Zn(CH_3)_2$, $Sb(CH_3)_3$, $Sn(CH_3)_4$, $Pb(CH_3)_4$, etc. These compounds are volatile, and so can be used to ascertain the quantivalence of the metals concerned.

It may be thought that since one atom of chlorine unites with one atom of hydrogen to form HCl, that chlorine could be used in a similar manner. This is also indeed the case, and the chlorides of many metals have been used for that purpose. Among the volatile chlorine compounds of the metals are the following :—

$HgCl_2$	$SbCl_3$	$SnCl_4$	$NbCl_5$	WCl_6
	$BiCl_3$	$TiCl_4$	$TaCl_5$	Al_2Cl_6
		VCl_4	$MoCl_5$	Fe_2Cl_6
			WCl_5	

Tungsten (W) unites with five atoms of chlorine, but it also unites with six, hence it is considered hexavalent. Molybdenum, which is very much like tungsten in general properties, is therefore also classed as a hexad although it does not form $MoCl_6$. Again, vanadium forms VCl_4, and therefore acts as a tetravalent element, yet in all its characteristic properties it is very unlike the other tetrads. It is, however, very closely allied in this respect to phosphorus and arsenic, and so has been classed with them as a pentad.

Nitrogen, and the other elements of its group (see Periodic Table), unite with three atoms of hydrogen, but phosphorus unites with three atoms of chlorine to form a stable compound which can be volatilized without decomposition, and also with five atoms to form the

compound PCl_5, which is unable to exist as a vapour, being decomposed at a temperature above its boiling-point into PCl_3 and Cl_2. Sulphur forms SCl_2, which readily decomposes into S_2Cl_2 and Cl_2 even at ordinary temperatures. Also, it is worth noting, that lead forms $Pb(CH_3)_4$, so that its chlorine compound may in all probability be represented by Pb_2Cl_4, and not as is usual by $PbCl_2$.

Unfortunately, the vapour densities of the chlorides are not easy to observe, since the temperature required in many cases is very high. So all we can say with respect to the compounds of the metals with chlorine is, that we can obtain the apparent quantivalence of the metal from them, but the few illustrations given will make it quite clear that it is not altogether a satisfactory method of determining the valency of an element.

Other Methods of determining the Combining Weights.—Some elements combine directly with one atom of hydrogen, and the combining weights of these elements can thus be directly compared with that of hydrogen. Then these elements in their turn can be used to find the combining weights of other elements which themselves do not unite directly with hydrogen. The element oxygen can be made use of in this manner, because a great many elements which form no hydrogen compounds, form oxides suitable for this purpose.

Carbon dioxide can be produced by burning a known weight of carbon in excess of oxygen. The weight of oxide so formed can be found, and from this the com-

bining weight of carbon calculated. The oxides of copper, lead, zinc, mercury, etc., can be used in a similar manner. Chlorides, bromides, and sulphides of some elements can be used for this purpose also.

Again, the combining weight may be found by the analysis of salts which break up when heated, so as to form a non-volatile basic oxide, and a volatile acid oxide. Carbonates, nitrates, and sulphates, all contribute suitable examples of this kind, and these can be made use of since the combining weights of carbon, nitrogen, and sulphur, are accurately known. The following example will illustrate how this method is used to obtain the combining weight of an element.

Suppose some calcium carbonate ($CaCO_3$) has been heated sufficiently to drive off the CO_2, and so reduce it to lime (CaO); then $CaCO_3 = CaO + CO_2$, represents the reaction which has taken place, and we have the proportion :—

The combining weight of Calcium + 16 (oxygen)	12 (carbon) + 32 (oxygen)	Weight of residual oxide	Weight of original $CaCO_3$, less weight of lime formed.

The last three terms are of course known, so the first can be at once calculated.

The combining weight of silver being known, it is possible to make use of the chlorides and bromides of elements, in order to find their combining weights. The method depends upon the fact, that silver chloride and silver bromide are insoluble compounds, and so all

that is necessary is to find the amount of silver required to take the place of the element which is united with the chlorine, or bromine, as the case may be. Thus, suppose the combining weight of sodium is required. Then common salt (NaCl) could be used for this purpose. A solution, (in pure water), containing a known quantity of NaCl is prepared, and silver nitrate solution is added until no further precipitate is formed. Then

Combining weight of sodium + chlorine (known) . Combining weight of silver (known) + chlorine (known) . . Weight of NaCl used (known) . . Weight of silver chloride formed (known)

and from this we can calculate the combining weight of sodium.

Isomorphism.—Another property which has been of extreme importance in indicating those elements which bear a true analogy to one another, and so has been used indirectly in atomic weight estimations, is that known as isomorphism. As the word itself indicates, this science deals with similarity of crystalline forms. Many crystalline substances have the same general form of crystal, that is, so far as number of faces, and arrangement of axes are concerned, but the angle which one face makes with another often varies slightly in similar crystals of different compounds. Thus, for example, calc spar ($CaCO_3$) takes the form of a rhombohedral crystal in which the angle is 105° 8′; magnesite ($MgCO_3$) crystallises in a similar form with an angle 107° 10′,

while calamine ($ZnCO_3$) crystals also have the form of rhombohedra, but the angle for these is 107° 40′.

It is usually found, that the more closely the shapes of the crystalline compounds approach one another so far as their detailed form is concerned, the more nearly allied are the substances contained in the crystals, so we should expect zinc to be more analogous to magnesium, than magnesium is to calcium, and this is actually found to be the case. Now all compounds of the alkali metals formed with the halogens, when they assume the crystalline form, do so either as cubes, or octahedra. All these compound substances contain the same number of atoms in their molecules, which again is found to be the universal rule with true isomorphic substances. If a solution of ferrous sulphate ($FeSO_4$) is mixed with a solution of cupric sulphate ($CuSO_4$), and the combined solution is evaporated down so as to obtain crystals from this mixture, these crystals will be found to contain both iron and copper salts. This phenomenon was first observed by Le Blanc in 1784, and was further developed, as was the whole science of isomorphism, by Mitscherlich in 1819, and subsequent years. This power to form homogeneous crystals from mixed solutions is one of the most direct and important methods of detecting a real analogy between two substances, and their true isomorphism. Again, one substance which is isomorphic with another, may help to induce crystallisation from solutions of the latter, when placed in those solutions in the form of a

crystal. This is well illustrated by placing a crystal of potash alum ($KAlS_2O_8 12H_2O$), into a solution of chrome alum ($KCrS_2O_8 12H_2O$). The crystal of potash alum is colourless, but very soon after it has been placed in the solution, it becomes covered with a violet-coloured layer of chrome alum, and the crystal continues to grow by the superposition of layers of the other alum in this manner. Such solutions are usually said to form " overgrowths " on the crystal.

The way in which it has been possible by a study of isomorphic substances, to help to establish a reliable system of atomic weights will be best appreciated by reference to an instance in which such a study could be used for that purpose.

The atomic weight of copper in the early part of the nineteenth century was taken to be 63·4, while that of silver was thought to be 216·6. These metals form sulphides, which are isomorphic with one another, and hence should have the same molecular constitution. Yet on the basis of the atomic weights just given, the composition of those sulphides should be represented by the formulæ Cu_2S, and AgS, respectively. If we accept the fact that these substances are truly isomorphic, and that the formula of copper sulphide is Cu_2S, then by analogy that of silver sulphide must be Ag_2S. This means that the atomic weight of silver must be changed from 216·6 to 108·3, which is of the same order as that found by more recent determinations. If the principles of isomorphism are accepted, it is at once apparent how

useful such a knowledge becomes, merely as a check upon other methods of ascertaining the molecular composition of compounds, and the atomic weights of the elements. By such means we can connect potassium with rubidium, cæsium with thallium, thallium with indium, while potassium may also be compared with sodium, sodium with lithium, and lithium with silver; silver in turn with copper, and the latter with nickel, cobalt, iron, etc. Thus, while the actual number of isomorphic substances in any one group may be small, the groups are so inter-connected one with the other, that by this means it becomes possible to link together the great majority of the elements. It is unfortunate, however, that all the elements cannot be so connected, and that more particularly, since hydrogen is one of the exceptions. As this is the case the atomic weights found by this method cannot be directly referred to hydrogen as unity, but its place has to be taken by some element the atomic weight of which is well established. This, perhaps, is not so great a defect after all, since it has been decided by the International Committee to refer the atomic weights to oxygen as 16, and not hydrogen as 1. It may be as well to point out also, that instances do occur in which substances crystallise in similar form, and yet they are not true isomorphic compounds. It is then that a knowledge of overgrowths, and the formation of homogeneous crystals from mixed solutions, enables one to settle the question. Sometimes, too, a group of elements can replace a single

element in a crystal; a good example of this is the compound radical (NH_4), which, as is well known, can replace potassium in many of its compounds. Now the chemical, electrolytic, and crystallographic values of the equivalents sometimes agreed, but very often disagreed, and it was not until 1858, when Cannizzaro first clearly explained the principles on which the determination of the atomic weights of the elements depend, that uniformity in this respect became possible. He insisted upon the fact, that the atom is the smallest portion of an element which is capable of entering into combination with other elements to form compounds; and this led to the disuse of equivalents, and the adoption of the present system of atomic weights.

There are many other methods of gaining information with respect to the relative magnitudes of the atomic weights of the chemical elements, some of which will be mentioned in subsequent chapters. Enough has been said here, to make it quite clear that no sound information on this subject was possible in those early days of chemistry, when experiments were considered almost entirely from the qualitative standpoint.

It should also explain in some degree, the very vague nature of some of the work on this subject which appeared in the early part of the last century; not only were different units taken as the standard of reference, but often no distinction was made between the terms, atomic weight, and equivalent, as will be seen in the following pages.

CHAPTER II

EARLY ATTEMPTS AT CLASSIFICATION

A. Prout's Hypothesis.—During the years 1815 and 1816 two anonymous communications appeared in the *Annals of Philosophy*.[1] These were afterwards known to be the work of Prout. In these papers he set forth his ideas on the constitution of matter, so far as the elements then known were concerned. The following are the opening phrases of the first of these communications. "The author of the following essay submits it to the public with the greatest diffidence; for though he has taken the utmost pains to arrive at the truth, yet he has not that confidence in his abilities as an experimentalist as to induce him to dictate to others far superior to himself in chemical acquirements and fame. He trusts however that its importance will be seen and that some one will undertake to examine it, and thus verify or refute its conclusions. If these should be proved erroneous, still new facts may be brought to light, or old ones better established, by the investigation, but if they should be verified, a new and interesting light will be thrown upon the whole science of Chemistry."

He then proceeded to state that his observations were

[1] *Annals of Philosophy*, vi., 1815, p. 321; vii., 1816, p. 113.

chiefly founded on the doctrine of volumes, as first generalised by M. Gay Lussac.

He calculated the atomic weights of the following elements in terms of hydrogen as unity.

Calculated from Specific Gravity		*Substances stated from Analogy, but of which we are yet uncertain*	
Hydrogen	1	Aluminium	8
Carbon	6	Magnesium	12
Nitrogen	14	Chromium	18
Phosphorus	14	Nickel	28
Oxygen	16	Cobalt	28
Sulphur	16	Tellurium	32
Calcium	20	Copper	32
Sodium	24	Strontium	48
Iron	28	Arsenic	48
Zinc	32	Molybdenum	48
Chlorine	36	Manganese	56
Potassium	40	Tin	60
Barium	70	Bismuth	72
Iodine	124	Antimony	88
		Cerium	92
		Uranium	96
		Tungsten	96
		Mercury	100
		Lead	104
		Silver	108
		Rhodium	120
		Titanium	144
		Gold	200

Not only is the absence of fractions in these results at once apparent, but also the fact that in very many

cases the results are sub-multiples of the accepted atomic weights. Prout called attention to the equality of the atomic weights of the three magnetic metals, iron, cobalt, and nickel (28), and also to the fact that their weight was just double that of nitrogen From this he concluded, that substances having the same atomic weights resemble one another in properties, and can combine more readily with one another. This was the first attempt to recognize any relationship between the atomic weights of the elements, and their characteristic properties. The numbers he obtained are all multiples of four, with the exception of those for carbon (6), Phosphorus (14), nitrogen (14), and barium (70), and these are all divisible by 2. On this account, he said, it appeared as if some element of higher atomic weight than hydrogen (1) had modified the elements in some way, and he made the suggestion that the modifying agent was probably oxygen (16); and from this he was led to offer the opinion that all the other elements are compounded of hydrogen and oxygen. In his second paper he put forward the idea that the element hydrogen is the " first matter " of the ancients. His own words on this point are, " If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous state to represent the number of volumes condensed into one; or, in other words the number of the absolute weight of a single volume of the ' first matter ' which they contain, which is extremely probable, multiples in weight must always indicate multiples

in volumes, and *vice versâ;* and the specific gravities, or absolute weights of all bodies in the gaseous state, must be multiples of the specific gravity, or absolute weight of the 'first matter,' because all bodies in a gaseous state which unite with one another, unite with reference to their volume." Thus the idea of a 'primary form' of matter from which all the chemical elements have been built up was once again put forward, and in one form or another it has remained with us ever since.

Thomas Thomson took up Prout's theory, and so warped did his own ideas on this subject become, that he actually compiled a set of atomic weights in which it would seem his main object was to obtain such numbers as would fit in with the theory; accuracy being considered as a matter of quite secondary importance. In the meantime, Berzelius,[1] by keeping an open mind, and adhering strictly to the results of his experimental work, published a set of atomic weights widely differing from those issued by Thomson, and of a fairly accurate nature. Such a fascination, however, has any theory which aims at explaining many different phenomena by a common cause, that we are not surprised to find Marignac (1860), with very distinct leanings towards Prout's hypothesis. Stas had by that time obtained a series of atomic weights for many elements in terms of hydrogen as unity; and his numbers certainly did not

[1] "Ueber die Bestimmung der relativen Anzahl der einfachen Atome in chemischen Verbindungen." *Pogg. Ann.* vol. viii. pp. 1-24 and 177-190.

favour the idea that all the other elements were compounded of hydrogen. Yet Marignac tried to explain how it came about that these numbers differed from whole numbers. His own words on this subject as taken from pp. 105-106 [1] are :—" We are able then to say of Prout's law, that which we can say of the laws of Mariotte and Gay-Lussac relative to variations of the volumes of gases. These laws, long considered as absolute, have been found to be inexact when subjected to experiments of so precise a nature as those of M. Regnault, M. Magnus, etc. Nevertheless, they will always be considered as expressing natural laws either from the practical point of view, for they allow the changes of volume of gases to be calculated in the majority of cases with a sufficiently close approximation, or even from the theoretical point of view, for they most probably give the normal law of changes of volume, when allowance has been made for some perturbing influences which may be discovered later, and for which it may also be possible to calculate the effects. We may believe that the same is true with respect to Prout's law ; if it is not strictly confirmed by experiment, it appears nevertheless to express the relation between the atomic weights of simple bodies (elements) with sufficient accuracy for the practical calculations of the chemist, and perhaps also the normal relationship which ought to exist among these weights, when allowance is made for some perturbing causes,

[1] " Rapports réciproques des Poids atomiques." Geneva, Bibliothèque universelle, vol. ix., 1860, pp. 97 *et seq.*

the researeh for which should exercise the sagaeity and imagination of ehemists. Should we not, for example, quite in keeping with the fundamental principle of this law, that is to say in admitting the hypothesis of the unity of matter, be able to make the following supposition, to which I attach no further importanee, than that of showing that we may be able to explain the diseordance which appears to exist between the experimental results and the direct consequenees of this principle? May we not be able to suppose, that the unknown cause (probably differing from the physieal and chemical agents known to us), whieh has determined certain groupings of the primordial matter so as to give birth to our simple ehemical atoms, and to impress upon each of these groups a special character, and peeuliar properties, has been able at the same time to exereise an influenee upon the manner in which these groups of atoms obey the law of universal attraction, so that the weight of eaeh of them is not exactly the sum of the weights of the primordial atoms whieh constitute it?"

Lothar Meyer (1896) eonsidered that it was quite conceivable that, after all, the atoms of all, or many of the elements, may consist chiefly of hydrogen as the primordial matter. He tried to explain the discrepaneies between the numbers obtained for the atomic weights and whole numbers, by assuming that the ether also enters into the eomposition of the elements, and that this ether may not after all be devoid of weight.

On the other hand, the numbers obtained by Stas for

the atomic weights in terms of hydrogen as unity were so far in many cases from being whole numbers, that he was led to the conclusion that Prout's hypothesis was without any real foundation.

B. Doebereiner's Triads.—The earliest work on the grouping together of elements having atomic weights which either increased in arithmetical progression, or were of nearly equal magnitude, appeared in 1829.[1]

Doebereiner in this communication called attention to the fact, that certain closely allied elements could be arranged in groups of three, and that their atomic weights as so arranged, were in arithmetical progression Thus :—

$$\frac{\text{Chlorine (34·470)} + \text{Iodine (126·470)}}{2} = \text{Bromine (80·470)},$$

the number so obtained for bromine differing only very slightly from that obtained by Berzelius (78·383). He did not consider that fluorine belonged to the same group as chlorine, etc., although it was a member of the same salt-forming class ; rather, it seemed to belong to a closely allied group, in which the two remaining elements necessary to complete the triad had not been discovered.

Other instances of the same kind given by him are :—

$$\frac{\text{Calcium (356·019)} + \text{Barium (956·880)}}{2} = \text{Strontium (656·449)}.$$

Found 647·285.

$$\frac{\text{Lithium (195·310)} + \text{Potassium (589·916)}}{2} = \text{Sodium (392·613)}.$$

Berzelius found 390·897.

[1] *Pogg. Ann.* 15, 1829, pp. 301 *et seq.*

In these cases the actual numbers given by Doebereiner have been quoted, and are the atomic weights referred to oxygen = 100.

$$\frac{\text{Sulphur (32·239)} + \text{Tellurium (129·243)}}{2} = \text{Selenium (80·471).}$$

Found 79·263.

In this also the numbers are as given by him, but are referred to hydrogen as unity.

He further pointed out, that if we consider the power which these elements possess of entering into combination with others to form salts, we find in the cases of potassium, sodium, and lithium; and of barium, strontium, and calcium, that the power of chemical attraction increases with increasing atomic weights; while the converse is true with respect to chlorine, bromine, and iodine.

The elements oxygen, hydrogen, nitrogen, and carbon, were looked upon by him as exceptions to the general rule, notwithstanding the fact that the atomic weight of nitrogen is the arithmetical mean between those of carbon and oxygen, and so in this way these three elements could be looked upon as forming a triad. The reason he gave for this was, that one was not able to find any analogy between these three elements.

In some cases two elements were grouped together by him, and the third looked upon as a possible new element. Instances of this kind are phosphorus and arsenic, and boron and silicon. Notwithstanding the fact that his main idea was that the analogous elements

could be arranged in groups of three, he was quite prepared to consider iron, manganese, nickel, cobalt, zinc, and copper, (the oxides of which Mitscherlich had already declared to be isomorphic), as forming a group by themselves, on account of the difficulty he found in grouping them as triads. Platinum, iridium, and osmium; silver, lead, and mercury, form two other triads. Whether tin ought to be classed with cadmium; antimony with bismuth; and gold with tungsten, or tungsten with tantalum; and what were the elements required to complete the triad in each case, he did not venture to guess.

Work on similar lines to this was carried out by many observers during the next thirty years, and some of these efforts at classification we shall next briefly consider.

C. In 1850 PETTENKOFER,[1] in a paper entitled "Ueber die regelmässigen Abstände der aequivalentzahlen der sogenannten einfachen Radicale. Eine Reclamation gegenüber Hrn Dumas Aequivalentgewichten der einfachen Körper," pointed out that it was not at all certain that the so-called elements were what they were represented to be, for the atomic weights of the elements differed in many cases by 8, or some multiple of 8, and so the elements might prove to be compound bodies, built up of the same simple body, or it might be, bodies. The following examples given by Pettenkofer, in which the numbers refer to the chemical

[1] Liebig's "Annalen," 105, pp. 187 *et seq.*

equivalents, will indicate what appeared to him sufficient cause for the ideas he put forward.

Lithium 7; sodium 23 (7 + 16); potassium 39 (23 + 16); magnesium 12; calcium 20 (12 + 8); strontium 44 (20 + 24); barium 68 (44 + 24).

The differences in the above instances, even when the most accurate atomic weights were used, were considered by him to so closely approximate to 8, or some multiple of 8, that it could not be looked upon as a mere coincidence. In some cases, as for example, carbon 6; boron 11 (6 + 5), and silicon (Kiesel) 21 (11 + 10), a similar kind of relationship appeared to exist, but here the difference was 5, or some multiple of 5.

These facts, together with the analogy which they suggest between the atoms of the so-called elements, and the series of organic molecules, in addition to the knowledge of the manner in which such compound radicals as ammonium and cyanogen, are often able to act as elements in forming compounds, led Pettenkofer to the conclusion which has been stated.

D. In 1853 Dr J. H. Gladstone,[1] in a paper on "The Relations between the Atomic Weights of Analogous Elements," says that the following remark, "We see that bodies which present the same properties, up to a certain point, have certain relations between their atomic weights," which was due to Berzelius,[2] led him to consider the question. His object was to illustrate this

[1] *Phil. Mag.* (4), 5 pp. 313 *et seq.*

[2] "Traité de Chimie," vol. iv.

statement, to show the extent of its truth, and to draw certain analogical inferences tending to the proper understanding of such a fact. The following is a list of the elements with their atomic weights which he made use of in compiling this paper.

1 Hydrogen
4·7 Glucinum
6 Carbon
6·5 Lithium
8 Oxygen
10·9 Boron
12 Magnesium
13·7 Aluminium
14 Nitrogen
16 Sulphur
19 Fluorine
20 Calcium
21·3 Silicon
22·4 Zirconium
23 Sodium
25 Titanium
26·7 Chromium
27·6 Manganese
28 Iron
29·5 Cobalt
29·6 Nickel
31 Phosphorus
31·7 Copper
32·6 Zinc
35·5 Chlorine
39·2 Potassium
39·5 Selenium
43·8 Strontium
46 Molybdenum
47 Cerium
47 Lanthanum
50 Didymium
52·2 Rhodium
52·2 Ruthenium
53·3 Palladium
56 Cadmium
58 Tin
59·6 Thorium
60 Uranium
64·2 Tellurium
68·5 Barium
68·6 Vanadium
75 Arsenic
80 Bromine
92 Tungsten
98·7 Platinum

99	Iridium	127·1	Iodine
99·6	Osmium	129	Antimony
100	Mercury	184	Tantalum
103·7	Lead	197	Gold
108·1	Silver	208	Bismuth

The numbers given in this table will be seen to differ, in a large number of cases, from those now accepted, hence it is necessary to give them, in order to be able to follow the arguments set forth, many of which would not of course apply, if the true atomic weights were used.

He called attention to the number of the elements, with atomic weights grouped about the values 28, 52, and 99, and then gave the following grouping of the elements which he acknowledged to have obtained from Gmelin's "Handbook of Chemistry," vol. ii. The figures indicating the atomic weights were not given in the original table, which occurs on page 1 of Gmelin's work.

	O							N								H				
	8							14								1				
F	Cl	Br	I													L	Na	K		
19	35	80	127													6	23	39		
	S	Se	Te													Mg	Ca	Sr		Ba
	16	39	64													12	20	44		68
		P	As	Sb							G	Er	Y	Tr		Ce	Di	La		
		31	75	129							5	—	—	—		47	50	47		
			C	B	Si								Zr	Th		Al				
			6	11	21								22	60		14				
		Tl	Ta	Nb	Pe	W						Sn	Cd	Zn						
		35	184	—	—	92						58	56	33						
					Mo	V	Cr		U	Mn	Co	Ni	Fe							
					46	69	27		60	28	29	30	28							
							Bi	Pb	Ag	Hg	Cu									
							208	104	108	160	32									
						Os	Ru	Ir	R	Pl	Pd	Au								
						100	52	99	52	99	53	197								

The numerical relationships which he considered as brought to light by this arrangement, are of three kinds :—(*a*) The atomic weights of the analogous elements may be the same ; (*b*) they may be in multiple proportions, or, (*c*) they may differ by certain definite increments. To illustrate the first, we have chromium 26·7, manganese 27·6, iron 28, cobalt 29·5, and nickel 29·6 ; also palladium 53·3, rhodium 52·2, and ruthenium 52·2 ; platinum 98·7, iridium 99, and osmium 99·6 ; then cerium 47, lanthanum 47, and didymium 50. The metals of each of these groups are associated in nature, and have similar properties, and Gladstone was of the opinion, that although the equivalent numbers obtained for the members of any one of the groups were so nearly alike, it was not to be expected that more accurate experimental work would show that their equivalents were equal.

To illustrate the groups in which the atomic weights are in multiple proportion, he mentioned the following. The platinum group (99), has double the palladium group (53), and again, gold (197) is the twin double of the platinum group. The following pairs of elements are also given : boron (10·9), silicon (21·3) ; and oxygen (8), sulphur (16).

The atomic weights of a large group of metals which form acid oxides insoluble in water, likewise exhibit this property. Thus—

		Accepted equivalent.
Titanium .	$2 \times 11{\cdot}5 = 23$	25
Molybdenum	$4 \times 11{\cdot}5 = 46$	46

		Accepted equivalent.
Tin . .	$5 \times 11{\cdot}5 = 57{\cdot}5$	58
Vanadium .	$6 \times 11{\cdot}5 = 69$	68·6
Tungsten .	$8 \times 11{\cdot}5 = 92$	92
Tantalum .	$16 \times 11{\cdot}5 = 184$	184

Silicon, although similar to titanium, was not included in this list, as its atomic weight (14·2) did not conform to the arrangement. The metals, the atomic weights of which are in multiple proportion, are not as a rule found together in nature.

Lastly, in the third group, where we have elements with atomic weights and properties intermediate between those of two other elements, we once again meet the triads. Such are :—

Alkalies :—Lithium 6·5, Sodium 23, Potassium 39·2 ;
Alkaline Earths :—Calcium 20, Strontium 43·8, Barium 68·5 ;
Halogens :—Chlorine 35·5, Bromine 80, Iodine 127·1 ; and the
Sulphur Group :—Sulphur 16, Selenium 39·5, Tellurium 64·2.

The elements of the last two groups generally occur together in nature. These groups were regarded as analogous to the series of homologous bodies in organic chemistry, which may be illustrated by :—

hydrogen (1), methyl (15), ethyl (29) ; for $\frac{1 + 29}{2} = 15$.

If $a = 1$ and $x = 14$, then these three, and the members of the series with higher molecular weights, may be represented by the algebraical series a ; $a + x$; $a + 2x$, etc.

Similarly, in the series lithium (6·5), sodium (23), and potassium (39·2); if a = Li = 6·5, x = 16·3, then a = lithium = 6·5; $a + x$ = sodium + 6·5 + 16·3 = 22·8. And $a + 2x$ = potassium + 6·5 + 2 (16·3) = 39·1 and so on. The equivalents of the group phosphorus (31), arsenic (75), and antimony (129), exhibit no relationship to one another. Other points which were noted are:— Bismuth has apparently no analogues. Alumina is usually classed with the earths, but some of its compounds are isomorphic with compounds of the iron group, and the equivalent of aluminium is one-half that of the members of the iron group. Glucina is an analogous earth, and the equivalent of glucinum is half that of aluminium (?). Some of the properties exhibited by lead, ally it to the family of alkaline earths, but there is apparently no numerical relationship; in other of its properties it resembles silver, but here again there is no relationship between the equivalents.

In conclusion, Gladstone remarks:—"It is against all probability that, by mere chance, whenever with one exception close analogy of properties exists, there exists also numerical relationship."

E. In 1854 Professor Cooke [1] of Harvard University gave the most complete classification depending upon the atomic weights of the elements, which had up to that time appeared. He considered that the division of the elements into groups of three (triads) was only a very partial view to take of the subject. These triads are

[1] *American Journal of Science and Art* (2), 17 pp. 387 *et seq.*

only parts of a series, which is similar in all respects to the series of homologues so well known in organic chemistry, in which the difference between the atomic weights of the members of the series is a multiple of some whole number. He classed all the elements into six series in each of which a different number may be said to be the characteristic of the series, and he considered that the numerical relationships made clear by his tables, included all the others which had up to that time been brought forward. He gave strong arguments against the method then existing, of dividing the elements artificially into metals and metalloids, a system by which in books of chemistry, arsenic, antimony, and bismuth, in spite of their close analogies to phosphorus, are described in different parts of the volume. At the same time pointing out how his classification into six series would remedy this defect. The want of some fundamental property common to all the elements, the law of whose variation was fully known, on which to base a correct classification of the element, was keenly felt; and it was argued that since chemistry presents us with no such property, we must base our classification on general analogies. The most fundamental of all the chemical properties was considered to be crystalline form, yet a classification based on isomorphism is acknowledged to be a defective one, for while it most certainly brings together the allied elements, it also groups together those which have no other properties in common except their crystalline form. Again, the

mode in which the elements combine seems a fundamental property, but here also elements possessing widely different chemical properties are brought into the same group. A classification which exhibited the natural affinities of the elements, would of course include both these, yet, if such a classification be adopted, other less fundamental properties must not be disregarded. For example, many physical and chemical properties which cannot be exactly measured should be taken into account; such are the properties which enable chemists to group together carbon, boron, and silicon, although they cannot be proved to be isomorphous, and are not generally thought to form similar compounds. The six series of Cooke's table were arranged so as to carry out the ideas which have just been set forth. He said of this table, "It corresponds entirely to the series of homologues in organic chemistry. In the group of volatile acids, homologues of formic acid, for example, we have a series of compounds yielding similar derivatives, and producing similar reactions, and many of whose properties such as boiling- and melting-points, specific gravities, etc., vary as we descend in the series, according to a determinate law. From formic acid, a highly limpid, volatile, corrosive fluid, the acids become less and less volatile, less and less fluid, less and less corrosive; first, oily, then fat-like, and finally hard, brittle solids like wax.

As is well known the composition of these acids varies in the same way, and the variations follow a regular

law, so that by means of a general symbol we can express the composition of the class. This symbol for volatile acids may be written $(C_2H)O_3,HO + n(C_2H_2)$. This description applies, word for word, *nominibus mutatis*, to each of the six series of chemical elements."

In the series the elements resemble one another in other respects than those given above, in particular, they are isomorphous, and many of the properties vary in a regular way as we descend the series. Take, as an example, the elements contained in the Eight Series, viz. : oxygen, fluorine, cyanogen, chlorine, bromine and iodine. Oxygen is a gas, fluorine is also a gas, and so is cyanogen, but the latter can easily be condensed to a liqnid ; bromine is a fluid, and iodine a solid under ordinary conditions. From cyanogen downwards the solubility in water of these elements decreases. Their atomic weights can all be represented by the general formula 8 + n9, in which we may consider the 8 to represent $(C_2H)O_3,HO$, as it does the atom of oxygen, and 9 to represent the (C_2H_2). To what it is that the 9 actually corresponds, Cooke was unable even to suggest, but hoped it might nltimately be brought to light. He gave detailed reasons for including fluorine with the other halogens, and likewise argued, that not only from considerations of atomic weight, but also on account of other analogies, cyanogen, though a compound radical, should be in this series. Since oxygen was recognized to present as strong an analogy with sulphur as with chlorine, and since not only from the stand-

point of analogy, but also from atomic weight considerations, it appeared to be the nucleus of all the first three series, it was placed at the head of each. In fact, when the atomic weight of an element was included in the general formula of any series, it was looked upon as an argument for including the element in that series.

The atomic weights used by Cooke were taken for the most part from the last volume of Liebig & Kopp, *Jahresbericht* for 1852; exceptions to this are indicated by the initial letter of the name of the observer, and these were taken from Weber's "Atomgewichts Tabellen."

The deviation of theoretical from observed values are considered to be, in the majority of cases, well within the limit of experimental error, but there were cases where the deviation was greater than could be so accounted for. As a rule, the experimental atomic weights of the highly active elements exceeded the theoretical, and the greater the activity the greater the difference. The unit of atomic weight which is used, is the double atom of hydrogen, but in the three series, the nucleus is the weight of a single atom, so that the unit here is one-half that employed in the other series.

The numbers to the left of the table (isomorphs) indicate the crystalline systems; thus: (1) Monometric, (2) Dimetric, (3) Trimetric, (4) Monoclinic (5) Triclinic, and (6) Hexagonal. The atomic weights which are underlined are twice the accepted value.

The 3 Series . . . general formula I + n3.

Isomorphs.		Homologues.		Atomic Weights.		
				Theoretical.	Observed.	Value of n.
3	1					
		Hydrogen	H_2O	1	1	0
	LiCl	Lithium	LiO	13	13	4
	NaCl	Sodium	NaO	46	46	15
NaO,So_3	KCl	Potassium	KO	79	78·4	26
Affiliations.						
AgO,SO_3	..	Silver	AgO	217	216·2	32

The 9 Series.

Isomorphs. 3	Isomorphs. 1	Homologies 8+n9.								Atomic Weights. Theoretical.	Observed.	Value of n.
	Cu_2O	...	Oxygen	HO	...	...	...	...	...	8	8	0
		KF	Fluorine	HF	...	...	...	...	...	17	18·8B	1
		KCy	Cyanogen	HCy	CyO	...	...	..	...	26	...	2
KO,ClO_7	Cu_2Cl	KCl	Chlorine	HCl	ClO	ClO_3	ClO_4	ClO_5	ClO_7	35	35·5	3
		KBr	Bromine	HBr	BrO ?	...	...	BrO_5	...	80	80	8
		KI	Iodine	HI	IO	...	...	IO_5	IO_7	125	126·9M.	13
Affiliations.												
	$KOCrO_3$	...	...	Chromium	...	...	...	...	...	Cr_2O_7	53	53·4	5
KO,Mn_2O_7	KO,MnO_3	...	...	Manganese	...	...	...	...	...	Mn_2O_7	53	55·2	5
				Osmium	...	...	...	OsO_4	...	...	98	99·4	10
				Gold	...	...	AuO_3	...	AuO_5 ?	...	197	197	21

The 8 Series (4 + n8) or (8 + n8).

Isomorphs.							Homologues.					Atomic Weights.		
6	4	3		2	1							Theoretical.	Observed.	Value of n.
					PbO	Cu_2O	Oxygen	HO	HO_2	...	...	8	8	0
		KO,SO_3	FeS_4	...	PbS	Cu_2S	Sulphur	HS	HS_2	SO_2	SO_3	16	16	1
		KO,SeO_3	...	...	PbSe	...	Selenium	HSe	...	SeO_2	SeO_3	40	39·6B	4
				$PbOMoO_3$	...	...	Molybdenum	...	...	MoO_2	MoO_3	44	6	5
Te	...	...	...	...	PbTe	...	Tellurium	HTe	...	TeO_2	TeO_3	64	64·1B	7
							Vanadium	...	...	VaO_2	VaO_3	68	68·5B	8
	$FeOWO_3$	...	...	$PbOWO_3$	...	...	Tungsten	...	...	WO_2	WO_3	92	92	11
	$FeOTaO_3$	...	...	...	...	...	Tantalum	...	...	TaO_2	TaO_3	188	184	23
Affiliations.														
As	...	...	$Fe_2(AsS_2)$	...	...	...	Arsenic	...	...	...	...	148	150	18
		$KOMnO_3$	...	...	...	...	Manganese	...	...	...	MnO_3	28	27·6	3

The 6 Series (8 + n6).

Isomorphs.					Homologues.					Atomic Weights.		
6	3		1							Theoretical.	Observed.	Value of n.
					Oxygen	...	...	...	...	8	8	0
					Nitrogen	NH_2	NH_3	NO_3	NO_5	14	14	1
	$NaOPO_5+4HO$	...	...	P	Phosphorus	PMe_2 / PH_2	PMe_3 / PH_3	PO_3	PO_5	32	31	4
As	$NaOAsO_5+4HO$	...	AsO_3	As	Arsenic	$As.Me_2$	AsH_3	AsO_3	AsO_5	74	75	11
Sb	...	SbS_3	SbO_3	...	Antimony	...	$SbMe_3$ / SbH_3	SbO_3	SbO_5	128	129	20
Bi	...	BiS_3	...	...	Bismuth	...	$BiAe_3$ / BiP_3	BiO_3	BiO_5	206	208	33
					Affiliations.							
					Chromium	...	...	CrO_3	...	26	26·7	3
					Vanadium	...	...	VaO_3	...	68	68·5	10

THE 5 SERIES (6 + n5).

Isomorphs.	Homologues.			Atomic Weights.		
1				Theoretical.	Observed.	Value of n.
C	Carbon	CO_2	...	6	6	0
	Boron	...	BO_3	11	10·9	1
	Silicon	...	SiO_3	21	21·3	3
		Affiliations.				
Ti	Titanium	TiO_2	...	26	25·2	4

F. In 1857 Professor ODLING,[1] who was professor at the Royal Institution, 1868-1873, sent two papers to the *Philosophical Magazine*, in which he propounded his ideas relative to the natural grouping of the elements. In his classification he was guided by what he calls "the totality" of the characteristic properties of the elements. By this is meant, that in grouping the elements, those elements should be placed together which, in the great majority of their properties, compounds, and reactions, exhibit similarities; although it might so happen that certain compounds of one may differ from corresponding compounds of the others, in some of their general properties.

He divided the elements into thirteen groups, as shown in the accompanying table. It will however at once be seen that one of the main ideas underlying the classification, is the possibility of forming triads.

[1] *Phil. Mag.* (4), 13, pp. 423 *et seq.*, 480 *et seq.*

Odling pointed out in all cases, a great number of analogies between the elements which are grouped together, and also between the compounds of those elements ; a brief mention will here be made of the more interesting only.

Groups I., II., III., and IV., he designated the chlorous elements, and the order given is that of descending order with respect to their acid properties.

In group I. the elements have one marked property in common, namely, that of combining with hydrogen atom to atom. No change takes place in volume when this combination is brought about, and the resulting compounds are all very powerful acids. There is a well-marked gradation in properties for the elements chlorine, bromine, and iodine, but fluorine is separated from the others by certain of its characteristic properties. The atomic weight of fluorine is very nearly equal to that of chlorine divided by 2.

In group II. one atom of each of the elements has the power to unite with two hydrogen atoms, so as to form either a neutral or a weak acid compound. When union takes place with hydrogen there is a diminution in volume equal to one-third the total volume before combination. Sulphur, selenium, and tellurium, show a marked gradation in properties, but oxygen while resembling the others in some respects, yet appears to bear the same kind of relation to them as fluorine does to the other members of the first group ; also, the atomic weight of oxygen is just one-half that of sulphur, as

	Group I	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.
	Mean difference 44	Mean difference 48	Mean difference 44	Mean difference 16	Mean difference 16	Mean difference 24	Mean difference 20?
	Fluorine 19	Oxygen 16	Nitrogen 14				
Triads	Chlorine 35·5	Sulphur. 32	Phosphorus 31	Boron 14·5	Lithium 6·5	Calcium 20	Magnesium 12·16
	Bromine 80	Scandium 79·2	Arsenic 75	Silicon 28·5	Sodium 23	Strontium 43·8	Zinc 32·5
	Iodine 127	Tellurium 128	Antimony 120	Titanium 48·4	Potassium 39	Barium 68·5	Cadmium 55·7
	242·5	239·2	226	91·4	68·5	132·5	100·36
	$\frac{242·5}{3}=80·8$	$\frac{239·2}{3}=79·7$	$\frac{226}{3}=75·33$	$\frac{91·4}{3}=30·46$	$\frac{68·5}{3}=22·8$	$\frac{132·5}{3}=44·1$	$\frac{100·36}{3}=33·45$
			Bismuth 213	Tin 117·6			

	Group VIII.	Group IX.	Group X.	Group X.	Group XI.	Group XII.	Group XIII.
	Mean difference 28	Mean difference $14=\frac{28}{2}$	Mean difference 2	Mean difference 2	Mean difference 24	Mean difference 4	
		Aluminium 13·7					
Triads	Glucinum 4·7	Zirconium 33·6	Iron 28	Chromium 26·3	Molybdenum 46	Mercury 100	Palladium 53·2
	Yttrium 32	Cerium 46	Nickel 29·5	Manganese 27·6	Vanadium 68·5	Lead 103·6	Platinum 98·6
	Thorium 59·6	Uranium 60	Copper 31·75	Cobalt 29·5	Tungsten 92	Silver 108	
	96·3	139·6	89·25	83·4	206·5	311·6	
	$\frac{96·3}{3}=32·1$	$\frac{139·6}{3}=46·5$	$\frac{89·25}{3}=29·75$	$\frac{83·4}{3}=27·8$	$\frac{206·5}{3}=68·8$	$\frac{311·6}{3}=103·8$	
					Tantalum 184		Gold 196·6

This table is the same in principle as that of Odling, and is arranged so as to show the triads at a glance. The calculations show the close agreement of the atomic weights of the middle elements with the mean values for the three in each group.

fluorine is about one-half that of chlorine. In group III., the elements possess the power to unite with three atoms of hydrogen, or three atoms of chlorine. In the case of ammonia (NH_3), there is a diminution when union takes place between the nitrogen and hydrogen, equivalent to one-half the original volume of the gases. Bismuth is not known to form bismuth hydride (BiH_3), but the others form hydrides which are alkaline, rather than acid, in their properties. Nitrogen bears the same relation to the elements of this group, as oxygen and fluorine do to their respective groups. Bismuth is inverse in its relationship as compared with nitrogen. Thus the atomic weight of nitrogen (14) is rather less than half that of phosphorus (31), while the atomic weight of bismuth (213) is rather less than twice that of antimony (120). The relationship in this respect appears still closer, if we consider the ratios $\frac{14 \times 2}{31}$ and $\frac{213}{120 \times 2}$; for these differ only by ·0153.

Odling gave reasons for considering the elements of group IV. capable of forming compounds by uniting with four atoms of chlorine (MCl_4). In this group the numerical sequence in the atomic weights is not so clearly marked, but he pointed out that the numbers given for silicon and titanium were not to be regarded as fixed.

The elements in the following groups (V.-XIII.) are to be regarded as of a basic nature. Group V.

contains the easily fusible, soft, volatile metals, all of which have a low specific gravity. They all possess the power to decompose water at all temperatures, and are easily combustible. Each forms only one class of salts, and nearly all their salts are soluble in water, and resist decomposition by heat. The metals contained in group VI. are also soft and easily fusible; they likewise are able to decompose water at all temperatures. They easily oxidise even in dry air, and each metal is capable of forming only one class of salts. Group VII. contains soft, white, easily fusible metals which are malleable, and can also crystallize in the form of octahedra. They are easily oxidised in moist air, but their power to decompose water is much less than the metals of groups V. and VI., for although magnesium can slowly decompose boiling water, zinc requires a slight acidulation in order to be able to do so, and cadmium requires a much stronger acidulation. There are many numerical inter-relationships between the elements of groups V., VI., and VII., such for example as, Zinc (32·5) + Sodium (23) = Cadmium (55·7), and again, Lithium (6·5) + Sodium (23) + Potassium (39) = Barium (68·5). The elements classed in the next two groups (VIII. and IX.) were at that time insufficiently known, consequently he laid no stress upon the existence of these groups, although the elements in each were known to present certain analogies.

He was uncertain as to the proper arrangement of the elements of group X., and wondered whether they ought

to be placed in parallel series as in the table or in a converging series as

Chromium (26·3) Iron (28) Manganese (27·6),
Nickel (29·5) Cobalt (29·5)
Copper (31·75)

He endeavoured to show that copper belongs to the iron group, and that the elements iron, nickel, and copper, form a triad, and again, that the relationship of this group to the others, depends upon the isomorphism of their compounds. In group XI. the elements were not sufficiently well known to be able to affirm their association in a positive manner, still many analogies between them were known to exist, and there was a well-marked sequence in their atomic weights. The atomic weight of tantalum was thought to be exactly double that of tungsten.

The elements of group XII. exhibit many analogies, *e.g.* all are readily fusible, all can be volatilized, all crystallize in octahedra, and so on.

Although in the thirteenth group gold is associated with platinum, the advisability of such a step is questioned, and at the same time it is pointed out that palladium appears to be associated with rhodium, and ruthenium, by equality of atomic weights. Platinum is likewise associated with iridium and osmium in the same manner, and further, the double chlorides of these three elements are isomorphic.

The whole thirteen groups contain thirteen triads of similar elements. In the iron group there are

two sets of triads, and this is probably the case in other groups also, while in the last group the triad is incomplete. In each triad the middle element has properties, and atomic weight, which are a mean between those of the two other elements; while in several cases, there are elements associated with the triads, the atomic weights of which are either one-half that of the first member, or double that of the last. Odling also indicated the relationship between the atomic volumes in the case of the chlorine, sulphur, iron, and platinum groups; in which the atomic volumes of the elements of any group are equal; while in the sodium, calcium, zinc, and lead groups, there is a sequence in the values of the atomic volumes of members of each group. In only one case, that of the phosphorus group, does there appear to be no relationship between the atomic volumes, and this is attributed to the allotropism of phosphorus.

In 1864 [1] Professor Odling made a further attempt at classification. He first of all gave the atomic weights of sixty-one elements, and pointed out the marked continuity of the numerical series which represented their atomic weights, when they were arranged in order of magnitude; the only important gaps being between calcium (40) and titanium (50); zinc (65) and arsenic (75); didymium (96) and mobybdenum (104); tantalum (138) and tungsten (184); tungsten (184) and niobium (195); and bismuth (210) and thorium (231·5). Scan-

[1] *Quarterly Journal of Science*, Oct. 1864.

dium has since filled the first vacancy, gallium and germanium the second, radium has helped to bridge over the last, while a general rearrangement of the atomic weights has since taken place which alters altogether the significance of the other three instances given. He showed that in comparing the atomic weights of analogous elements, a number exceeding one-half the whole of the elements then known could be arranged in pairs having atomic weights showing differences of between 84·5 and 97. About one-half of these pairs were the first and last members of triads, and he thought it probable that this might be the case in all such instances, the other intermediate elements having yet to be discovered. On account of these triplet groups there also exist other pairs, the atomic weights of which differ by 48 about, and there are 10 other instances in which a difference of 16 exists between pairs of more or less analogous elements. He made the assertion that those elements whose resemblance to one another is most pronounced, have a difference of about 48 between their respective atomic weights, and the more nearly the difference approaches that number the closer the resemblance. Thus the difference between the atomic weights of cadmium and zinc is 47, and these resemble one another much more closely than zinc and magnesium, where the difference is 41, or again, antimony resembles arsenic much more closely than arsenic does phosphorus, and the differences between the atomic weights in these two cases are 47, and 44, respectively. The most

interesting feature of the communication is a table, in which analogous elements, having a difference of approximately 48 between their atomic weights, are placed on a certain level, while those with a difference of only 44 or 40, are placed on somewhat lower levels; for this table also indicates that valency is a periodic function of the atomic weight, although this was not actually so stated by Odling. He was impelled by the large number of instances in which 48, 44, 40, or 16, occurred as the difference between the atomic weights of analogous elements, to regard 4 as embodying in some fashion the unit of common difference, although at the same time the differences are only approximately multiples of 4, and there are instances of closely allied elements, between the atomic weights of which differences of 2, or some odd multiple of 2, or 1, or even 0 occur. He concludes with the following remarks :—

"Since many of the elements occupying analogous positions in different groups have closely approximating atomic weights, it is evident that the mere determination of the atomic weight of a newly discovered element assists us but very little in deciding to what group it belongs, but only indicates its position in the group; since *among the members of every well-defined group the sequence of properties and the sequence of atomic weights are strictly parallel to one another.*"

"Doubtless some of the arithmetical relations exemplified in the foregoing tables and remarks are simply accidental; but taken altogether, they are too numerous

and decided not to depend upon some hitherto unrecognized law."

Monads	Diff. 4	...	Br 80	I 127	...	...
	F 19	Cl 35·5	...	.	...	...
	Diff. 12	...	...	Ag 108		Au 196·5
	L 7	Na 23	...	...	...	Tl 203
	Diff. 16	K 39	Rb 85	Cs 133	...	...
Dyads	O 16	S 32	Se 80	Te 129	...	...
	Diff. 8	...	...	V 137	W 184	...
	Diff. 8	...	Mo 96	...	...	...
	Diff. 4	Cr 52·5	...	...	...	...
	Diff. 8	...	Zn 65	Cd 112	...	Hg 200
	G 9	Mg 24	...	...	...	Pb 207
	Diff. 16	Ca 40	Sr 87·5	Ba 137	...	...
Triads	Diff. 4	...	As 75	Sb 122	...	Bi 210
	N 14	P 31	...	...	...	...
	Diff. 4	...	...	U 120	...	...
	B 11	Al 27·5	...	..	...	...
	Diff. 16	...	Ce 92	...	...	...
Tetrads	Diff. 8	...	...	Sn 118	...	...
	C 12	S. 28	...	...	...	...
	Diff. 12	...	Tr 89·5	Ta 138	...	..
	Diff. 8	Ti 50	...	...	Cb 195	Th 231·5

G. Dumas,[1] 1858, was the next to consider this question and his work is interesting since he used the equivalents of the elements as his standard of comparison, and not their atomic weights, and considered the main questions relative to the grouping of the elements, which had been put forward up to that time. He was first

[1] *Comptes Rendus*, 46, 1858.

The work of Dumas is given in this position since it was not until 1858 that his papers appeared in the *Comptes Rendus*, although he had some time previously laid his views before the British Association.

interested in the equivalents from the standpoint of Prout's hypothesis, and gave the following lists of elements as evidence on this question.

A.

Those with equivalents which are whole numbers, *i.e.* multiples of hydrogen.

1.	Oxygen	8
2.	Sulphur	16
3.	Selenium	40
4.	Tellurium	64
5.	Nitrogen	14
6.	Phosphorus	31
7.	Arsenic	75
8.	Antimony	122
9.	Bismuth	214
10.	Fluorine	19
11.	Bromine	80
12.	Iodine	127
13.	Carbon	6
14.	Silicon	14
15.	Molybdenum	48
16.	Tungsten	92
17.	Lithium	7
18.	Sodium	23
19.	Calcium	20
20.	Iron	28
21.	Cadmium	56
22.	Tin	59

B.

Those with equivalents which are multiples of one-half that of hydrogen.

1.	Chlorine	35·5
2.	Magnesium	12·5
3.	Manganese	27·5
4.	Barium	68·5
5.	Nickel	29·5
6.	Cobalt	29·5
7.	Lead	103·5

C.

Those with equivalents which are multiples of one-fourth that of hydrogen.

1.	Aluminium	13·75
2.	Strontium	43·75
3.	Zinc	32·75

He next drew attention to the comparison between nitrogen 14, phosphorus 31, arsenic 75, antimony 122, fluorine 19, chlorine 35·5, bromine 80, iodine 127, in that 14 + 108 = 122 ; 19 + 108 = 127 ; 14 + 61 = 75 ; and 19 + 61 = 80. Also, with the exception of chlorine, those on the lower line are 5 units larger than those above. Berzelius, who made a life study of the equivalents of the elements, was convinced that the figures representing the equivalents are connected by merely accidental relations, which disappear in proportion as the true values of the equivalents are more nearly obtained. The elements were on this account looked upon by him as being distinct, and independent of one another, their molecules having nothing in common except their fixity, their immutability, and their indestructibility. As previously stated, Dumas was in the first place deeply concerned as to whether Berzelius or Prout was correct, but decided at once that the question could not be approached by the numbers collected by Berzelius. The equivalents of chlorine and copper as at that time accepted, were marked exceptions to Prout's hypothesis, so, that although Dumas felt he could safely rely on the accuracy of the work of previous experimenters, he undertook the redetermination of the equivalents of these elements, and found that of chlorine to be 35·5, and that of copper to be between 31 and 32, but of his results in this latter case he did not feel certain. Hence the conclusion he arrived at was, that the equivalents of nearly all the elements are multiples by whole numbers

of the equivalent of hydrogen taken as unity, but that in the case of chlorine at least, the unit of comparison ought to be one-half the equivalent of hydrogen.

To consider the question whether the equivalents of any of the elements were exactly equal, or in the proportion 1 : 2, he mentioned first the elements molybdenum and tungsten. These are closely related so far as chemical and physical properties are concerned, yet their accepted equivalents were 48 and 92 respectively, which numbers do not bear any simple relationship to one another. Yet, he did not seem satisfied that such simple relationship did not exist between the equivalents in some cases, for he found the equivalents of oxygen and sulphur, in all his experiments, were to one another as 8 : 16. He likewise knew that Berzelius had found the equivalent of oxygen to differ from 8 by a small fraction, but practically accuses him of systematically denying the existence of such apparent relationships. Consequently, holding firmly by his own results, Dumas declared that elements do exist the equivalents of which are to one another in the ratio 1 : 2.

As instances of elements having the same equivalents, he mentioned chromium and manganese, for each of which the equivalent was found to be 26. But while believing that such relationships might exist between analogous elements, he pointed out that it may happen that such relations do not exist even for the most closely allied elements, although the numbers which represent their true equivalents seem very nearly to realise them.

On the question of triads he mentioned the following :

$$\frac{\text{Sulphur (16)} + \text{Tellurium (64)}}{2} = 40 \text{ (Selenium).}$$

$$\frac{\text{Lithium (7)} + \text{Potassium (39)}}{2} = 23 \text{ (Sodium).}$$

$$\frac{\text{Calcium (20)} + \text{Barium (68)}}{2} = 44 \text{ (Strontium).}$$

$$\frac{\text{Chlorine (35·5)} + \text{Iodine (127)}}{2} = 81{\cdot}25 \text{ (Bromine).}$$

In the last case the accepted equivalent of bromine being 80, it became absolutely certain that the equivalent of bromine was not the mean between those of chlorine and iodine, although these three elements are most closely allied, and, so far as properties are concerned, bromine is always intermediate between the other two. Hence, although for three bodies of the same family the equivalents of the intermediate element may be equal to the arithmetical mean of the equivalents of the extremes, there may on the contrary be most closely allied elements where no such relationship exists. The triad theory, therefore, could not be looked upon as a general one.

He next tried to show that the equivalents of those elements which belong to the same group (if we are careful to compare only those elements well known to belong to the same family), offer in the manner in which

they are built up, a marked analogy to the equivalents of organic radicals belonging to the same series.

Thus—$CH_4 = 16 = a$,

$C_2H_6 = 16 + 14 = a + d$,

$C_3H_8 = 16 + 2(14) = a + 2d$; and so on.

Iodine, bromine, chlorine, and fluorine, were the first to commend themselves for comparison in this way; and he proceeded to show that their equivalents can be built up as follows :—

a	19	Fluorine 19,
$a + d$	19 + 16·5	Chlorine 35·5,
$a + 2d + d^1$	19 + 33 + 28	Bromine 80,
$2a + 2d + 2d^1$	38 + 33 + 56	Iodine 127.

Again, for nitrogen, phosphorus, arsenic, antimony, and bismuth, we have :—

a	14	Nitrogen 14,
$a + d$	14 + 17	Phosphorus 31,
$a + d + d^1$	14 + 17 + 44	Arsenic 75,
$a + d + 2d^1$	14 + 17 + 88	Antimony 119,
$a + d + 4d^1$	14 + 17 + 176	Bismuth 207.

In the case of carbon, boron, silicon, and zirconium, since boron is represented by 11, silicon by 22, and zirconium by 33, silicon is the mean between the other two. The equivalents for the four substances seemed connected as follows :—

a	6	Carbon 6,
$a + d$	6 + 5	Boron 11,

$a + 3d$	$6 + 15$	Silicon 21,
$3a + 3d$	$18 + 15$	Zirconium 33.

In the group oxygen, sulphur, selenium, and tellurium, the values of a and d can both be taken as equal to 8 :—

So that a	8	Oxygen 8,
$2a$	16	Sulphur 16,
$5a$	40	Selenium 40,
$8a$	64	Tellurium 64,

could be used to represent these, although from analogy it would be better to write them as :—

a	8	Oxygen 8,
$a + d$	$8 + 8$	Sulphur 16,
$a + 4d$	$8 + 32$	Selenium 40,
$a + 7d$	$8 + 56$	Tellurium 64.

$8 = d$ can be used also for the following groups :—

a	12	Magnesium 12,
$a + d$	$12 + 8$	Calcium 20,
$a + 4d$	$12 + 32$	Strontium 44,
$a + 7d$	$12 + 56$	Barium 68,
$2a + 10d$	$24 + 80$	Lead 104 ;
And a	7	Lithium 7,
$a + 2d$	$7 + 16$	Sodium 23,
$a + 4d$	$7 + 32$	Potassium 39.

The difference of 8, or of multiples of 8 so used, Dumas compared with the frequently recurring difference of 14, which occurs in the organic compound radicals. He

agreed that many of the equivalents of the metals needed revision, but believed that the results he had obtained were favourable to Prout's hypothesis, except, that for certain elements, the numbers must be referred to a smaller unit than the equivalent of hydrogen. The progressions which have been given above were explained in the following manner. The first element in any one of the series, *e.g.*, fluorine, is looked upon as the determining factor with respect to the chemical characteristics of all the others coming after it in the same group. So that if we consider a as the first term of the progression, and d the relation between the terms; in any equivalent represented by $a + nd$, it is the a which gives the fundamental chemical character, and which fixes the class to which the element belongs; while the nd determines only the place which the element occupies in the group, and its peculiar properties.

This work of Dumas is more often referred to in brief accounts of the Periodic Law, and classifications of the elements, than that of Professor Cooke, yet it is quite clear that the latter deserves equal mention, for as a general system of classification it certainly surpasses that of Dumas.

All the attempts made prior to 1860, were unsuccessful in establishing a continuous system including all the elements, partly, because underlying the idea of classification of the elements according to their chemical and physical characteristic properties, there was also the

idea that it should be possible to build up these elements from one or more simpler forms; in fact, Cooke went so far as to insist on this as the determining factor, on which the inclusion of an element in any particular group should depend. This of course led to the formation and consideration of groups, as being more or less distinct one from another, and so prevented any periodic variation of properties, with increasing atomic weights, from being clearly marked.

So that, although any one with a knowledge of the Periodic Law as given by Mendeleeff, can, on glancing back at these first attempts, perceive in them the germs of that great final classification, yet up to 1860, no system had appeared which could claim to be looked upon as the direct forerunner of it. For this reason the works of De Chancourtois, and Newlands, both of which have some claim in this respect, are in this book, separated from these more crude attempts, and placed in a separate chapter as a kind of bridge, between them and Mendeleeff's work.

CHAPTER III

DE CHANCOURTOIS AND NEWLANDS

THERE seems no doubt that to a certain extent, the fundamental principle of the Periodic Law was foreshadowed by M. de Chancourtois. In this too he has a prior claim to that of Newlands, for his papers on the subject were handed in to the French Academy in April 1862, May 1862, and March 1863, while Newlands' first attempt did not appear until 1863. In his 1863 paper Chancourtois made the definite statement, "The properties of the bodies (elements) are the properties of number," and this he illustrated by his so-called Telluric Helix.

The claim of M. DE CHANCOURTOIS to having made any advance upon the ideas of Dœbereiner, Dumas, etc., in the classification of the elements, seemed for some time likely to be completely overlooked. Then P. J. Hartog gave a translation of his first communication to the Academy, which was entitled, "Sur un classement naturel des corps simples ou radicaux appelé vis tellurique." This appeared in *Nature*, 26th December 1889. Again, in 1891,[1] MM. Lecoq de Boisbaudran

[1] *Comptes Rendus*, 112, pp. 77 *et seq.*

and A. de Lapparent, tried to gain the recognition of priority for their compatriot. No account of the periodic law would therefore be complete which did not give some account of this attempt at systematic classification.

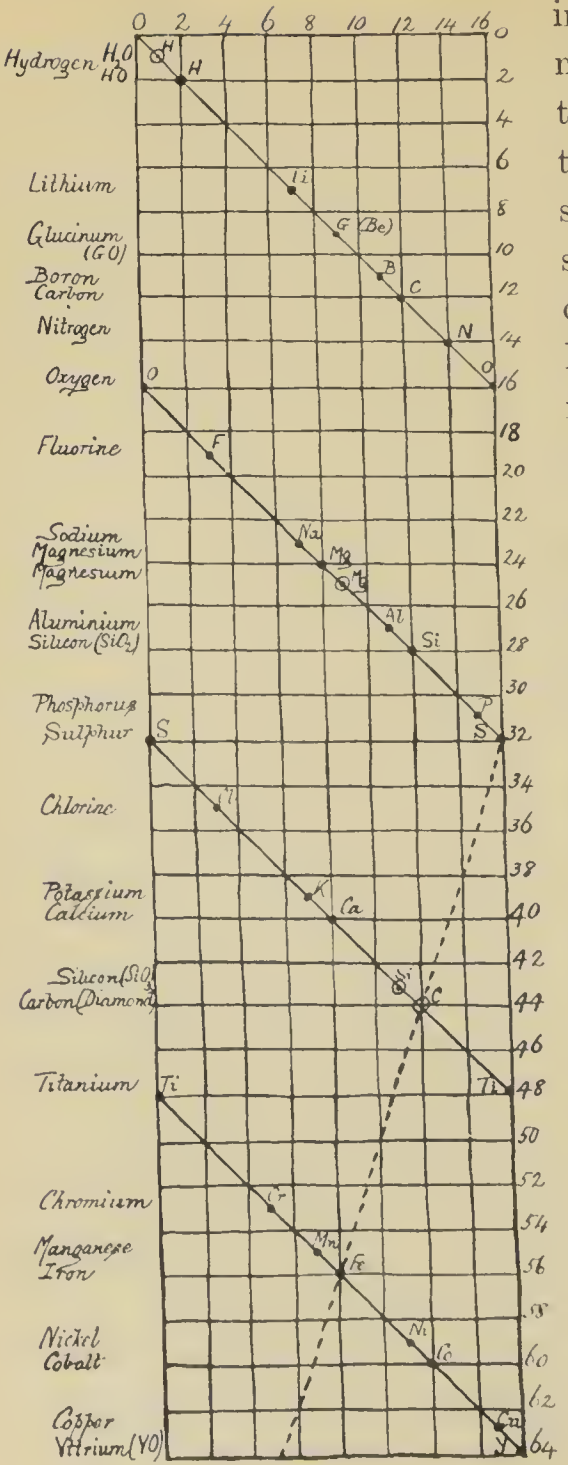
The fundamental idea of the Telluric Helix consists in plotting the values of the atomic weights along the generatrix of a vertical cylinder, the circular base of which is divided into 16 equal parts ; 16 was chosen since it represented the atomic weight of oxygen.

If now we trace upon this cylinder a helix, inclined at an angle of 45° to the axis, each point of this helix may be considered as the *characteristic point* of a simple body, the atomic weight of which is proportional to the corresponding length of the spiral. This may be read on the generatrix which passes through the point. This will be rendered more distinct by a reference to the accompanying figure which is a copy of that given by MM. Boisbaudran and Lapparent in the communication to which reference has already been made. The numbers used by Chancourtois were the combining weights which were adopted by Cannizzaro in 1858.

The diagram shows the cylinder developed for the elements of combining weights between those of hydrogen and tellurium. It is seen that oxygen, sulphur, selenium, and tellurium all lie on the same generating line, while calcium, iron, strontium, and uranium lie on the diametrically opposite line, and so on. From instances such as this Chancourtois concluded that " the relations between the properties of different bodies are mani-

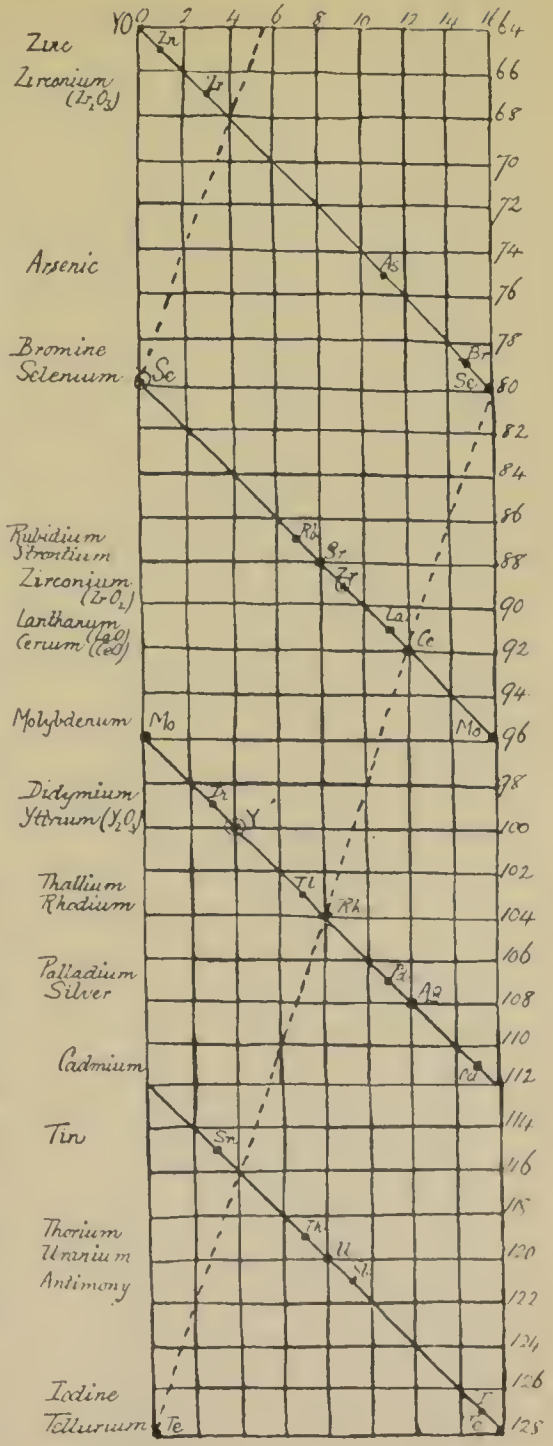
fested by simple geometrical relations between their *characteristic points*." Now, as the diagram is drawn on a cylinder, it is clear that more than one helix might be drawn so as to pass through several of the characteristic points of the elements. An example of this kind is shown by the dotted lines on the figure. From this he argued that "Each helix drawn through two *characteristic points*, and passing through several other points, or near them, brings out relations of a certain kind between their properties; likenesses and differences being manifested by a certain numerical order in their succession, for example immediate sequence, or alternation at various periods." The helices other than the main one at 45° are known as secondary helices.

The occurrence of carbon in a position indicating a combining weight of 44, is due to the fact that he used the atomic heats of sulphur and lead, in order to calculate the atomic weight of the diamond, the specific heat of the latter being known. Chancourtois seems to have been carried away with the idea, that the atomic weights could all be represented by whole numbers, and starting from this idea, he arrived at the conclusion that in the natural series, the differences between the atomic weights ought to be constant. On this account, when he perceived gaps in his list of elements he tried to fill the vacancies by imagining new varieties of the known elements, such as in the case of carbon, and these he called "caractères secondaires." Naturally, this often led to groupings being made in which elements were



included having no natural analogies to the remainder of the group. These secondaires are shown on the diagrams thus ⊙. He also thought it was possible to reproduce the series of the natural numbers, in the series formed by the numerical characteristics of the elements, supplemented by those of the compound radicals, such as cyanogen, ammonium, etc. In such a system the bodies which are truly elements might be represented by the prime numbers, and he gave a table containing twelve such elements.

He further conceived the idea that his series might be of use as a guide in researches on spectrum analysis, for he said, "Will not the relations of the different rays of the spectrum prove to be derived directly from the law of numerical characteristics, or *vice versâ*?" In his system, he gave a general formula $(n + 16n^1)$ for the numerical characteristics of the elements. In this n^1 is always to be an integer, and n was also always an integer in his calculations, although he stated that it need not be so.



By referring to the diagram the

reason for this will be at once apparent, for consider the elements on any generating line such as lithium (7), sodium ($7 + 16 = 23$), potassium ($7 + 2 \times 16 = 39$), manganese ($7 + 3 \times 16 = 55$), and so on.

Chancourtois might almost be said to have originated the idea of "Octaves," which is always associated exclusively with the name of Newlands, for in his first paper he remarked, "The development in a plane of the cylinder ruled into squares, with the circumference at the base divided into 16 equal parts, seems to me in a word, to be a 'stave' on which men of science after the fashions of musicians, will note down the results of their experimental or speculative studies, either to co-ordinate their work, or to give a summary of it in the most concise and clear form to their colleagues and the public"; or again, in 1863, when he spoke of "Direct developments of the system, which make apparent at the same time the approach of the actual series of the numerical characteristics, with the series of musical sounds, and with that of the bands and lines of the spectrum."

Newlands has often been spoken of as the discoverer of the Periodic Law, and as we consider his work we shall find some reason for this; yet, the extension of the work as due to Mendeleeff is so much in advance of Newlands' "Law of Octaves," as to merit the place now assigned to the former as the real discoverer of the law.

In his earlier communications,[1] Newlands arranged the elements into certain groups. In this he was guided by their chemical characteristics, rather than their physical properties, hence we find no distinction drawn between metals and non-metals. Like the earlier workers he used the terms "equivalent," and "atomic weight," as synonymous, and this at times leads to some confusion. He divided the elements into the following eleven groups :—

I. Metals of the Alkalies.		II. Metals of the Alkaline Earths.		III Metals of the Earths.		IV. Metals whose Protoxides are Isomorphous with Magnesia.	
Lithium	7	Magnesium	12	Beryllium	6·9	Magnesium	12
Sodium	23	Calcium	20	Aluminium	13·7	Chromium	26·7
Potassium	39	Strontium	43·8	Zirconium	33·6	Manganese	27·6
Rubidium	85	Barium	68·5	Cerium	47	Iron	28
Cæsium	123			Lanthanium	47	Cobalt	29·5
Thallium	204			Didymium	48	Nickel	29·5
				Thorium	59·6	Copper	31·7
						Zinc	32·6
						Cadmium	56

V. Halogens.		VI. Oxygen Group.		VII. Nitrogen Group		VIII. Carbon Group.	
Fluorine	19	Oxygen	8	Nitrogen	14	Carbon	6
Chlorine	35·5	Sulphur	16	Phosphorus	31	Silicon	14·20
Bromine	80	Selenium	39·5	Arsenic	75	Titanium	25
Iodine	127	Tellurium	64·2	Osmium	99·6	Tin	58
				Antimony	120·3		
				Bismuth	213		

[1] *Chemical News*, 1863 (Feb.).

IX.	X.	XI
Molybdenum 46	Rhodium . 52·2	Mercury . 100
Vanadium . 68·6	Ruthenium 52·2	Lead . . 103·7
Tungsten . 92	Palladium . 53·3	Silver. . 108
Tantalum . 184	Platinum . 98·7	
	Iridium . 99	

Making use of the numbers attached to the elements in the table the following relations given by him will be noticed :—

In Group I.—7 + 39 = 46 or 1 Lithium + 1 Potassium = 2 Sodium.
7 + 78 = 85 or 1 ,, + 2 ,, = 1 Rubidium.
7 + 117 = 124 or 1 ,, + 3 ,, = 1 Cæsium.
7 + 156 = 163 or 1 ,, + 4 ,, = (Element not yet discovered.)
7 + 195 = 206 or 1 ,, + 5 ,, = 1 Thallium.

In Group II.—$\frac{\text{Calcium } 20 + \text{Barium } 68{\cdot}5}{2} = 44{\cdot}25 = \text{Strontium.}$

In Group III.—Aluminium = 2 Beryllium or,

$$\frac{\text{Beryllium } 6{\cdot}9 + \text{Zirconium } 33{\cdot}6}{3} = 13{\cdot}5 \text{ (Aluminium).}$$

Again, zirconium 33·6 + 2 aluminium (27·4) = 61 = thorium ; while lanthanum and didymium have equivalents which are very nearly equal.

In Group IV.—$\frac{\text{Magnesium } 12 + \text{Cadium } 56}{2} = 34 = \text{Zinc,}$

$$\frac{\text{Cobalt } (29{\cdot}5) + \text{Zinc } 32{\cdot}6}{2} = 31{\cdot}05 = \text{Copper,}$$

$$\text{Iron } 28 = \frac{\text{Cadmium } 56,}{2}$$

$$\frac{\text{Iron } 28 + \text{Chromium } 26{\cdot}7}{2}$$

$= 27{\cdot}35 =$ Manganese, and lastly Cobalt = Nickel.

In Group V.—$\frac{\text{Chlorine } 35{\cdot}5 + \text{Iodine } 127}{2} = 81{\cdot}7 = \text{Bromine.}$

In Group VI.—$\frac{\text{Sulphur } 16 + \text{Tellurium } 64{\cdot}2}{2} = 40{\cdot}1 = \text{Selenium.}$

In Group VII.—$\frac{\text{Phosphorus } 31 + \text{Antimony } 120{\cdot}3}{2} = 75{\cdot}6 = \text{Arsenic.}$

In Group VIII.—(Tin 58 – Titanium 25) = 33 = 3 (Titanium 25 – Silicon 14·2).

In Group IX.—$\frac{\text{Molybdenum } 46 + \text{Tungsten } 92}{2} = 69 = \text{Vanadium.}$

Also Tungsten 92 = 2 Molybdenum 46; while Tantalum 186 = 4 Molybdenum 46.

In Group X.—The equivalents of the first 3 are equal, or very nearly so.

That of platinum is nearly equal to that of iridium; while each of the first 3 is nearly one-half those of the last two.

In Group XI.—$\frac{\text{Mercury } 100 + \text{Silver } 108}{2} = 104 = \text{lead.}$

In all this Newlands made no great advance upon the work of those Chemists mentioned in the preceding chapter. It has been given here in order that his work may be followed from the very beginning, and so in some measure the steps by which he was led up to the formulation of the 'law of Octaves,' may be appreciated.

He pointed out that in the case of the triads, if we deduct the lowest equivalent from that immediately above it, the numbers so obtained in many instances bear simple relations to each other. As examples of this we may take :—

Lowest.		Next.		Difference.
Magnesium	12	Calcium	20	8
Oxygen	8	Sulphur	16	8
Carbon	6	Silicon	14·2	8·2
Lithium	7	Sodium	23	16
Fluorine	19	Chlorine	35·5	16·5
Nitrogen	14	Phosphorus	31	17

In these the differences approximate to 8, or 8×2. A simple relationship although not such an obvious one, he found to exist between the numbers obtained by subtracting the equivalents of the lowest, from those of the highest members of the triads. Such for example are the following :—

Lowest.		Highest.		Difference.	
Lithium	7	Potassium	39	32	1×8
Magnesium	12	Cadmium	56	44	
Molybdenum	46	Tungsten	92	46	Approximately
Sulphur	16	Tellurium	64·2	48·2	6×8
Calcium	20	Barium	68·5	48·5	
Phosphorus	31	Antimony	120·3	89·3	Approximately
Chlorine	35·5	Iodine	127	91·5	12×8

Again, in the platinum family, group X., the difference between the equivalent of the highest member, iridium 99, and that of the lowest, rhodium 52·2, is 46·8, which approximates to 6×8. This led to the conclusion that it was most probable these two elements formed the extremes of a triad, of which the mean had not then been discovered.

These numerical relationships were most probably deduced in imitation of the work of Dumas, but even a

superficial glance is sufficient to make it plain, that the so-called approximations are much too divergent from the truth to be of any real interest. Newlands himself admitted, that many of the relations were more apparent than real, although at the same time, he thought some were of a more satisfactory nature. In July 1864 he arranged the elements in the form of a table so as to show the relations between them with which he was familiar at that time.

In this table he classed boron with gold, because gold was looked upon as trivalent, although it was also known to be monovalent, and in this his classification was at fault. The following is the table as given by him :—

			Triads.				
			Lowest Term.	Mean Term.	Highest Term.		
I.	...	Li 7	+17=Mg 24	Zn 65	Cd 112	...	
II.	...	Bo 11	...	...	...	Au 196	
III.	...	C 12	+16=Si 28	...	Sn 118	...	
IV.	...	N 14	+17=P 31	As 75	Sb 122	+88	Bi =210
V.	...	O 16	+16=S 32	Se 79·5	Te 129	+70	Os =199
VI.	...	F 19	+16·5=Cl 35·5	Br 80	I 127	...	
VII	Li 7	+16=Na 23	+16=K 39	Rb 85	Cs 133	+70	Tl =203
VIII.	Li 7	+17=Mg 24	+16=Ca 40	Sr 87·5	Ba 137	+70	Pb=207
IX.	...	...	Mo 96	V 137	W 184	...	
X.	...	...	Pd 106·5	...	Pt 197	...	

In this table the atomic weights are used, and not the equivalents of the elements. These weights increase from left to right along any horizontal line, and from top to bottom in the vertical columns. A number of well-known elements, such as silver, copper, iron, etc. not included in the table.

He connected the element silver with the metals of the alkalies.

Since Lithium (7) + Potassium (39) = 2 Sodium (46),
Lithium (7) + 2 Potassium (78) = Rubidium (85),
2 Lithium (14) + 3 Potassium (117) = Cæsium (131),
Lithium (7) + 5 Potassium (195) = Thallium (202),
And 3 Lithium (21) + 5 Potassium (195) = 2 Silver (216); again,
Sodium 23 + Rubidium 85 = Silver 108, and

$$\frac{\text{Rubidium } 85 + \text{Cæsium } 133}{2} = 109 = \text{Silver nearly.}$$

There is some amount of cross classification in the table, lithium being connected with groups I., VII., and VIII., and magnesium with I. and VIII. There is also room left for elements which may be discovered, such as the mean terms of the triads in groups III. and X.

Attention is called to the fact that the atomic weights (Newlands used the term equivalents) of some members of the same group, differ by 16, or some multiple of 16, very approximately, as is shown in the table. That is by an amount equal to the atomic weight of oxygen; and he drew a comparison between this and Prout's hypothesis, that the difference between the atomic weights of the elements, are always multiples of that of hydrogen.

It was in August 1865 that the well-known "Law of Octaves" was first put forward by Newlands, and the table to illustrate this was then given in the following form—

H	1	F	8	Cl	15	Co and Ni	22		Br	29	Pd	36		I	42	Pt & Ir	50
Li	2	Na	9	K	16		Cu	23		Rb	30	Ag	37		Cs	44		Tl	53
G	3	Mg	10	Ca	17		Zn	25		Sr	31	Cd	38	Ba & V		45		Pb	54
B	4	Al	11	Cr	19		Y	24	Ce & La		33	U	40		Ta	46		Th	56
C	5	Si	12	Ti	18		In	26		Zr	32	Sn	39		W	47		Hg	52
N	6	P	13	Mn	20		As	27	Di & Mo		34	Sb	41		Nb	48		Bi	55
O	7	S	14	Fe	21		Se	28	Ro & Ru		35	Te	43		An	49		Os	51

The numbers 1 to 56 simply indicate the order in which the elements would lie if placed in the ascending order of their atomic weights. In the chief part of the table it will be seen that the numbers increase in order from the top to the bottom of the vertical columns.

In certain cases however, notably in the last vertical column, transpositions had to be made, in order to bring those elements into line with others belonging to the same family. The members of the same family are found along the same horizontal line, and as a rule, therefore, the numbers which indicate these elements, will differ by 7, or some multiple of 7. The relation between elements of the same family, are, as a matter of fact, just the same as that which in music exists between the notes at the extremities of one or more octaves; hence it was, that he designated this the "Law of Octaves."

In some cases the same number was used to indicate two distinct elements; the reason being, that the atomic weights of those elements were then looked upon as equal. In March 1866 when Newlands brought the subject before the notice of the Chemical Society, the rule given by him was "The numbers of analogous elements, when not consecutive, differ by 7 or some multiple of 7; the phrase, 'when not consecutive,' is introduced for the purpose of embracing certain analogous elements whose atomic weights are consecutive, for example, the series containing chromium 19, manganese 20, iron 21, nickel and cobalt 22, copper 23 and zinc 24."

The table as given appears eomplete, no spaee being left for any new elements which might be discovered later. This, as Dr Gladstone pointed out at the time, was an objeetion to the adoption of the elassification, sinee eæsium, thallium, indium, and rubidium, had been discovered only a few years before that time. This was not the only objeetion raised; some of those present, like Professor Foster, were tired of the many attempts at elassifieation, which up to that time had borne very little fruit. That gentleman asked Newlands in a joeular vein, "whether he had ever examined the elements aecording to the order of their initial letters?" He also further eondemned the arrangement, beeause manganese and ehromium were so widely separated by it; and likewise niekel and eobalt were separated from iron. In answer to his erities, Newlands replied that he did not believe the discovery of new elements, or any necessary revision of the atomie weights of the then known elements, would upset for any length of time the existenee of a simple relation between the elements, when they are arranged in order of their atomie weights. At the same time, he agreed it might be neeessary to alter the number (7) which separated analogous elements, to some higher figure, should a large number of new elements be diseovered.

If Newlands' octaves are rearranged as in the following table, in whieh the numbers refer to the horizontal lines in the table of octaves, and the Roman numerals to Mendeléeff's groups, it will be seen how very near

1	VII	2	1	3	II	4	III	5	IV	6	V	7	VI
H	...	Li	Li	Be	Be	B	B	C	C	N	N	O	O
F	F	Na	Na	Mg	Mg	Al	Al	Si	Si	P	P	S	S
Cl	Cl	K	K	Ca	Ca	Cr	—	Ti	Ti	*Mn*	V	Fe(8)	*Cr*
Co(8)Ni(8)	*Mn*	Cu	Cu	Zn	Zn	Y	—	*In*	—	As	As	Se	Se
Br	Br	Rb	Rb	Sr	Sr	*Ce La*	?Y	Zr	Zr	*Di Mo*	Nb	Ro(8) Ru(8)	*Mo*
Pd(8)	—	Ag	Ag	Cd	Cd	*U*	*In*	Sn	Sn	Sb	Sb	Te	Te
I	I	Cs	Cs	Ba, V	Ba	*Ta*	?*Di*	*W*	*Ce?*	Nb	—	*Au*	—
Pt(8) Ir(8)	—	*Tl*	—	*Pb*	—	*Th*	—	*Hg*	—	Bi	—	Os(8)	—
			—	...	—	...	?*Er*	...	*La?*	...	*Ta*	...	*W*
			Au	...	*Hg*	...	*Tl*	...	*Pb*	...	Bi	...	—
									Th	...	...	...	*U*

The periodic table as given by Mendeléeff, August 1871,[1] has been used for this comparison.

[1] *Annalen*, Supplement viii. p. 133, 1872.

Newlands came to the discovery of the Periodic Law. The elements, the names of which are printed in italics, would have to be transposed in order that the two tables

Symbol.	Number.	Equivalent.	*Equivalent* ÷ Number.	Symbol.	Number.	Equivalent.	*Equivalent* ÷ Number.
H	1	1	1	Br	29	80	2·758
Li	2	7	3·5	Rb	30	85	2·833
G(Be)	3	9	3	Sr	31	87·5	2·823
B	4	11	2·75	Zr	32	89·5	2·797
C	5	12	2·4	Ce	33	92	2·788
N	6	14	2·33	Di	34	96	2·824
O	7	16	2·286	Ro	35	104	2·971
F	8	19	2·375	Pd	36	106·5	2·958
Na	9	23	2·555	Ag	37	108	2·919
Mg	10	24	2·4	Cd	38	112	2·947
Al	11	27·5	2·5	Sn	39	118	3·026
Si	12	28	2·33	U	40	120	3
P	13	31	2·385	Sb	41	122	2·975
S	14	32	2·286	I	42	127	3·024
Cl	15	35·5	2·367	Te	43	129	3
K	16	39	2·437	Cs	44	133	3·023
Ca	17	40	2·353	Ba	45	137	3·044
Ti	18	50	2·778	Ta	46	138	3
Cr	19	52·5	2·763	W	47	184	3·915
Mn	20	55	2·75	Nb	48	195	4·062
Fe	21	56	2·667	Au	49	196	4
Co	22	58·5	2·659	Pt	50	197	3·94
Cu	23	63·5	2·761	Os	51	199	3·902
Yt	24	64	2·667	Hg	52	200	3·846
Zn	25	65	2·6	Tl	53	203	3·83
In	26	72	2·769	Pb	54	207	3·833
As	27	75	2·778	Bi	55	210	3·818
Se	28	79·5	2·839	Th	56	238	4·25

might coincide. Those indicated thus Fe(8) belong to the group VIII. of the periodic table.

Shortly after the publication, in August 1865, of the table to illustrate the Law of Octaves, Newlands published another paper in which he tried to show that the various relations which had been pointed out by

Doebereiner, Dumas, and others, as existing between the equivalents of the elements, were the direct result of his Law of Octaves. The accompanying table as given by him, helps to illustrate this, and is also instructive as giving the equivalents (really atomic weights) on which his table of octaves was based.

In the last column of the table it will be noticed that the numbers are approximately constant for a certain range of the elements. Thus, from number 4 to 17, its value is about 2·5; from 18 to 34 it is 2·75; from 35 to 46, 3; and from 47 to 56 the value approaches 4.

From this it is evident, that since the rate of increase of the equivalents corresponds more or less closely to that of the numbers which are assigned to the elements, anything which is true respecting the latter, would within limits be likewise true with respect to the former. Thus, if the number of one element happens to be the mean between those of two other elements, its equivalent will also approximate to the mean of the equivalents of the other two. As an example of this, titanium number 18, is the mean between fluorine number 8, and selenium number 28; now the equivalent of titanium is 50, and this is approximately the mean of the equivalents of fluorine 19, and silenium 79·5.

According to Newlands the triads of Dumas, etc., were only approximations, and not real triads. In his idea the real triads were to be found among those analogous elements the numbers of which differ from one another by 7 or some multiple of 7.

He further argued that this also explains why we obtain a constant (16) by deducting the equivalent of the lowest member of a group from that of the element immediately above it, for if instead of taking those elements whose numbers differ by 7, we perform a similar calculation with the equivalents of those elements having numbers differing by say 8 or 9, we should obtain as a difference, a number which will be quite as constant as the one obtained by using the equivalents of analogous elements. In other words, the difference of 16 merely expresses the average difference for an interval of seven elements in the lower part of the scale of equivalents.

Although both the telluric helix, and the Law of Octaves, were distinct advances upon anything that had preceded them, inasmuch as a distinct periodic variation of properties among the elements, when arranged in the order of their atomic weights, is apparent; yet they can hardly claim to have been the origin of the periodic law as now accepted.

Mendeléeff was of course indebted to those who, like Dumas and others, had made attempts at classifying the elements, but his work embodied so many new ideas, and the old ones were reset in such a manner, that what had been previously at the best but a very disjointed array, was transformed into a wonderfully and marvellously connected system. It is worthy of note that Mendeléeff stated he was not acquainted with the work of Newlands at the time of the publication of his periodic

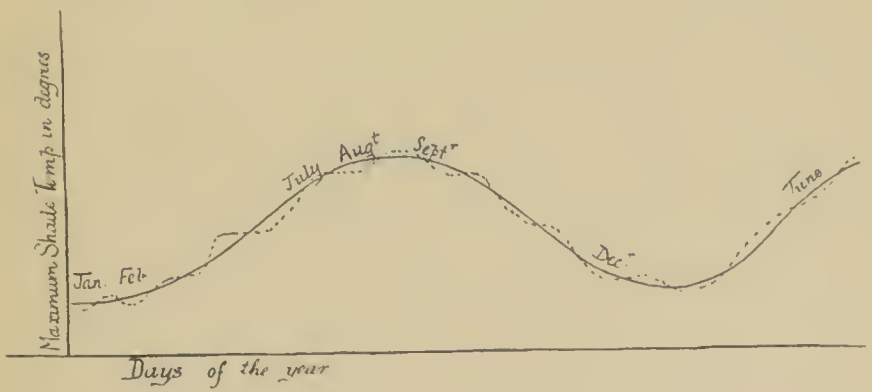
law, but that he at the same time recognized that it contained certain germs of that law. In the next chapter we shall consider the work of Mendeléeff together with that of his German contemporary, Lothar Meyer.

CHAPTER IV

MENDELÉEFF AND LOTHAR MEYER

Before proceeding further it is advisable to obtain a clear idea of what is meant by a periodic variation, and in particular, what is the nature of the periodic variation which may be expected, in connection with the properties of the chemical elements, when they are considered in the ascending order of their atomic weights. Periodic changes are constantly going on in the universe. The constant change of the average temperature with the seasons, from summer heat, through an autumn of varying temperature to the cold of winter, then through the ever-increasing brightness of spring back to summer and so on. The changing phases of the moon, from new through half to full, and then through half to new, with its gradually increasing reflecting area turned towards the earth until it appears as a circle of light, and then the gradual decrease in light area to point of invisibility, are familiar examples. In a climate like that of England, the general terms as stated above, by no means express exactly what takes place, for very often changes of temperature at any particular place occur, which are both sudden, and to a certain extent, unex-

pected. Hence if the days of the year were plotted as abscissæ, and the maximum shade temperatures as ordinates, the curve formed by joining the points so obtained would not be a smooth one rising to its maximum in July and August, and sinking in a uniform manner to a minimum in December and January. Rather, the curve would present a great many irregularities, and the general curve showing the periodic variation of temperature, can only be obtained by drawing a smooth curve so as to leave the irregularities uniformly distributed with respect to it, as in the accompanying diagram—

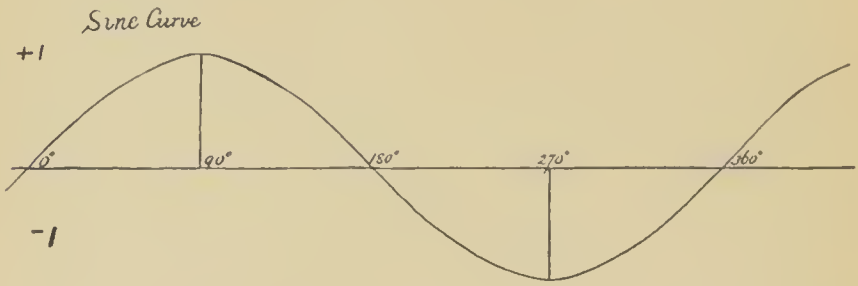


For all this, and although the maxima and minima in successive years may differ, we look upon the changes of temperature during the year, as of a periodic nature.

In the second illustration, if we plot the days as abscissæ, and the amount of surface of the moon visible each day as ordinates, we should get a more uniform

curve rising from minimum to maximum and returning to minimum again in about twenty-nine days.

The best example of a periodic curve, is that which represents the value of the sine of a gradually increasing angle, when the values of the angle in degrees are plotted as abscissæ, and the numerical values of the sines as ordinates. Here the values of the ordinates vary from + 1 to − 1, as shown in the diagram.



Such a smooth periodic curve can only be obtained when we are dealing with the continuous function of some variable. Now the atomic weights of the elements do not increase in a continuous manner, so that if their values are plotted as abscissæ, and any other property of the elements is used for plotting the ordinates, the curve formed by joining the points so obtained will not be a continuous one like the sine curve, since there are gaps between successive elements where no points can be fixed. But, if in the temperature curve we imagine the points to have been obtained from observations made at somewhat irregular intervals, and these observations to have extended over a period of some years, we

should then have the kind of curve with which we have to deal when the properties of the elements are plotted against their atomic weights. There are well-marked maxima and minima in each case, yet, just as it would be extremely unwise for any one to predict the maximum shade temperature on any given day simply from a knowledge of its periodic changes, so it would be exceedingly risky to predict the degree in which an element will exhibit a certain property, simply from a knowledge of the periodic variations of that property with increase of atomic weight. Yet, when some other data are at hand with respect to the weather immediately preceding, it is often fairly safe to hazard a guess at the prospect of the temperature exceeding, or being less than the average, especially if one is familiar with the result of similar conditions at the same time of year, on former occasions. Similarly, it has been possible to predict the general properties of elements from a knowledge of the atomic weight of those elements, and the properties of the neighbouring elements in the table, as we shall see when dealing with the " Analogues " of Mendeléeff.

Mendeléeff's Periodic Law.—The system as given to the world of science by the late Professor Mendeléeff of St Petersburg in 1869, appeared just as soon as one could have expected, having regard to the progress of development of chemical knowledge. Many things, no doubt, in some measure helped to bring about the state of affairs which proved to be the natural forerunners of such a climax. It was during the sixties that the values of the

atomie weights of the elements were more definitely fixed; for example, in 1860, ehemists from all parts of the world met at Karlsruhe, in order to eome to some agreement with respeet to the definite numerical representation of the elements. Then again, by the elose of the sixties a great deal of information had been aeeumulated with respeet to the more rare elements; and their relationship one to another, and to the other groups of elements, had beeome better known. So, with plenty of detailed information with respect to the various elements, and a knowledge of the many previous attempts at elassification, it required but the master mind to produee a satisfaetory seheme, which should embrace all the then known elements, and also leave space for the admission of any whieh might be discovered later.

The first paper published by Mendeléeff dealing with this subjeet, was entitled "An attempted classification of the elements based on their atomie weights and ehemieal analogies." This appeared in the early part of 1869, and copies of it were distributed among well-known ehemists.

In Mareh of the same year he contributed a paper to the Russian Chemical Soeiety, in which a table of the elements was given. This appeared later in German [1] under the title "Ueber die Beziehungen der Eigensehaften zu den Atomgewichten der elemente"; but in this edition Mendeléeff's views of the subject were to some extent misrepresented. In this translation his views

[1] *Zeitschrift für Chemie*, 1869, p. 405.

were put as follows, "Die nach der Grösse des Atomgewichts geordneten Elemente zeigen ein *stufenweise* Abhänderung in den Eigenschaften." The word which has been rendered "stufenweise" (gradual—or step-wise), would have been more correctly interpreted by the word "periodische."

It is important at this stage, to consider the claims to priority of Mendeléeff and L. Meyer. For this purpose, the first table given by Mendeléeff will be considered in comparison with the one given by L. Meyer, slightly later in the same year. Meyer's paper in which his table appeared is dated December 1869, but did not appear in Liebig's *Annalen* until 1870.[1] This paper was entitled "Die Natur der Chemischen Elemente als Function ihrer Atomgewichte." There should be no doubt whatever, then, that the great Russian chemist was the first in the field, even if we had not the further confirmatory evidence that in his paper, Meyer quotes Mendeléeff's paper, which appeared in the *Zeitschrift für Chemie* for 1869. These tables were very different from the later one of Mendeléeff in general appearance, and yet there were a great many points in which the classifications were the same. The elements belonging to the same natural family will in both these earlier tables be found along the horizontal lines, and if the upper portion of Mendeléeff's table be placed in three separate columns, there is little to distinguish one table from the other. In other words, Meyer's table was simply a

[1] Liebig's *Annalen*, Supplement vi. and vii., p. 354, 1870.

modification of its predecessor, and no great progress had been made, although differences occur which will be noted later.

The following are the tables to which reference has been made :—

I. Mendeléeff's Table.

Russian Chemical Society, March 1869.

...	...	...	Ti 50	Zr 90	(?) 180
...	...	...	V 51	Nb 94	Ta 182
...	...	...	Cr 52	Mo 96	W 186
...	...	...	Mn 55	Rh 104·4	Pt 197·4
...	...	...	Fe 56	Ru 104·4	Ir 198
...	...	Ni =	Co 59	Pd 106·6	Os 199
H = 1	...	...	Cu 63·4	Ag 108	Hg 200
...	Be 9·4	Mg 24	Zn 65·2	Cd 112	...
...	B 11	Al 27·4	(?) 68	U 116	Au 197 (?)
...	C 12	Si 28	(?) 70	Sn 118	...
...	N 14	P 31	As 75	Sb 122	Bi 210
...	O 16	S 32	Se 79·4	Te 128 (?)	..
...	F 19	Cl 35·5	Br 80	I 127	...
Li 7	Na 23	K 39	Rb 85·4	Cs 133	Tl 204
...	...	Ca 40	Sr 87·6	Ba 137	Pb 207
...	...	(?) 45	Ce 92	...	...
...	..	(?) Er 56	La 94	...	...
...	...	(?) Yt 60	Di 95	...	...
...	...	(?) In 75·6	Th 118 (?)	..	...

[1] *Zeitschrift für Chemie*, p. 405, 1869.

II. Lothar Meyer's Table, *Deeember* 1869.[1]

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
...	B 11·0	Al 27·3	...	——	...	?In 113·4	...	Tl 202·7
...	...	...	——	...	——	...	——	...
...	C 11·97	Si 28	...	——	...	Sn 117·8	...	Pb 206·4
...	...	...	Ti 48	...	Zr 89·7	...	——	...
...	N 14·01	P 30·9	...	As 74·9	...	Sb 122·1	...	Bi 207·5
...	...	...	V 51·2	...	Nb 93·7	...	Ta 182·2	...
...	O 15·96	S 31·98	...	Se 78	...	Te (?) 128	...	...
...	...	...	Cr 52·4	...	Mo 95·6	...	W 183·5	...
...	F 19·1	Cl 35·38	...	Br 79·75	...	I 126·5	...	...
...	...	...	Mn 54·8	...	Ru 103·5	...	Os 198·6 ?	...
...	...	...	Fe 55·9	...	Rh 104·1	...	Ir 196·7	...
...	...	Co =	Ni 58·6	...	Pd 106·2	...	Pt 196·7	...
...	...	...	...	Rb 85·2	...	Cs 132·7	...	...
Li 7·01	Na 22·99	K 39·04	Cu 63·3	...	Ag 107·7	...	Au 192·2	...
...	...	...	...	Sr 89	...	Ba 136 78	...	...
(?) Be 9·3	Mg 23·9	Cu 39·9	Zn 64·9	...	Cd 111·6	...	Hg 199·8	...
...	...	...						

Difference between I. and II., and II. and III. about = 16.
,, III. to V, IV. to VI., V. to VII. varies about = 46.
,, VI. to VIII. and VII. to IX = 88 to 92.

[1] Liebig's *Annalen*, Supplement vii., 1870, p. 354.

By comparing the tables the following differences in classification will be noticed. In II. osmium occupies the position of platinum in I., and *vice versâ*, gold, not quicksilver, is classed with copper and silver. In I. gold is classed with aluminium and uranium. In II. beryllium and magnesium are classed with the alkaline earths, while in I. they are in the same horizontal line with zinc and cadmium, which elements together with mercury are formed into a separate group in II. Carbon is classed with lead in II. but in I. lead is classed with calcium. Thallium is placed in the sodium group in I., not so in II.

Meyer noted that similar properties recur in elements when the atomic weights are increased by 16 (see difference between columns II. and III), 46 (difference between III. and V., and IV. and VI., also between V. and VII) and 88 or 92 (as between columns VI. and VIII. and VII. and IX.). This however had been previously noted by Odling. Meyer likewise noted a periodic rise and fall of the valency, as for example is shown in :—

Univalent.	Bivalent.	Trivalent.	Quadrivalent.	Trivalent.	Bivalent.	Univalent.
Lithium Sodium	Beryllium Magnesium	Boron Aluminium	Carbon Silicon	Nitrogen Phosphorus	Oxygen Sulphur	Fluorine Chlorine

and so on.

At the meeting of the Russian Chemical Society held in March 1869, when his first table was published, Mendeléeff set forth his views on the subject, and it will be very instructive to consider these briefly, since they

contain the fundamental elements of the Periodic Law. They were as follows :—

I. When the elements are arranged in the ascending order of their atomic weights, it is at once apparent that elements having a given property occur periodically. This is well illustrated by the halogens chlorine, bromine, and iodine, for these elements though so similar in fundamental properties possess widely differing atomic weights.

II. Those elements which exhibit very similar chemical and physical properties have atomic weights of nearly the same magnitude, such as the group iron, nickel, and cobalt, all of which are magnetic ; or again their atomic weights increase regularly, such as is the case with the elements of the halogen group.

III. When the elements are arranged in the ascending order of their atomic weights, they also fall naturally into their proper order as regards their valency, thus monovalent sodium (23), divalent magnesium (24), trivalent aluminium (27), tetravalent silicon (28), pentavalent phosphorus (31), hexavalent sulphur (32) and heptavalent chlorine (35·5).

IV. Elements such as hydrogen, oxygen, nitrogen, etc., which are most widely distributed in nature have the smallest atomic weights. These elements are also characterised by exhibiting well-marked properties which make them quite distinct from the other elements. On this account he proposed to call hydrogen and those elements included in the second series of his table, " Typical Elements."

V. The character of an element is determined by the magnitude of its atomic weight.

VI. Many yet unknown elements may be looked for; in particular, elements the atomic weights of which would lie between 65 and 75, and whose properties are similar to those of aluminium and silicon, may be expected to be discovered.

VII. When the atomic weights of neighbouring elements in the table are known, the atomic weight of another element may sometimes be corrected. Thus the atomic weight of tellurium cannot be 128 as is supposed, but must lie between those of antimony 123, and iodine 127. Brauner later on found the atomic weight of tellurium to be 125 about, but the most recent list[1] still gives an atomic weight of 127·5 for tellurium, and it is thus higher than that of iodine (126·92).

Lastly VIII., when the atomic weight of an element is known, certain of its characteristic properties may be foretold.

In August 1871 Mendeléeff[1] drew up the table in a form which has been used ever since to illustrate the Periodic Law. As then given by him, it was as in the accompanying table :—

[1] *International Atomic Weights*, 1909.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
				RH_4	RH_3	RH_2	RH	
Series	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
1	H = 1							
2	Li 7	Be 9·4	B 11	C 12	N 14	O 16	F 19	
3	Na 23	Mg 24	Al 27·3	Si 28	P 31	S 32	Cl 35·5	
4	K 39	Ca 40	— 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56 Co 59 Ni 59 Cu 63
5	(Cu 63)	Zn 65	— 68	— 72	As 75	Se 78	Br 80	
6	Rb 85	Sr 87	(?) Yt 88	Zr 90	Nb 94	Mo 96	—100	Ru 104 Rh 104 Pd 106 Ag 108
7	Ag (108)	Cd 112	In 113	Sn 118	Sb 122	Te 125	I 127	
8	Cs 133	Ba 137	(?) Di 138	(?) Ce 140	—	—	—	
9	(—)	—	—	—	—	—	—	
10	—	—	(?) Er 178	(?) La 180	Ta 182	W 184	—	Os 195 Ir 197 Pt 198 Au 199
11	(Au 199)	Hg 200	Tl 204	Pb 207	Bi 208	—	—	
12	—	—	—	Th 231	—	U 240	—	

A full account of his views were published in German [1] under the title, "Die periodische Gesetz mässigkeit der chemischen Elemente," and the above table occurs in that account.

The Roman numerals which are placed at the head of the vertical columns indicate the groups into which the elements are divided. The complete table contains another group known as the zero group; this group was added later owing to the discovery of the elements of the argon type. These elements have little or no capacity for entering into combination with other elements, and on this account it seems natural to place their group in the table before group I. The elements in the twelve horizontal lines form the twelve series, those which occur on lines indicated by odd numbers being spoken of as the odd series, the others as the even series. The even series in three cases are extended by the elements belonging to the eighth group, but those of the odd series end always with group VII. When a series such as 5 consists of seven elements only, it is known as a short series or period, while the elements on lines 4 and 5 if taken together form a long, or large period. The elements which belong to the same group are much more closely allied as regards their general properties, when they all belong to the same kind of series, that is to say, are either all even, or all odd. Thus, chlorine (series 3), is much more nearly related to

[1] *Annalen*, Supplement viii., p. 133, 1872, Tables on pp. 149, 151.

bromine (series 5), and iodine (series 7), than it is to manganese (series 4), or even to fluorine (series 2).

There are certain other particulars in which the elements belonging to the even series differ from those which are placed in the odd series, and some of these are so well marked as to be worthy of note in this connection. Thus, as a rule, it is extremely easy to obtain in a free state the elements which belong to the odd series, while those belonging to the even series can be so obtained only with great difficulty. Naturally there are exceptions to such a general rule, but they are confined to the elements contained in group VIII., and the typical elements, carbon, nitrogen, oxygen, sodium, magnesium, aluminium, and silicon.

The elements of the even series only very rarely combine with organic radicals to form compounds, such as methides, ethides, etc.; while those of the odd series very readily form these compounds. The same is true with respect to the hydrides formed by the elements of groups IV., V., VI. and VII. (see Table, page 104). The elements of the even series, if we except carbon, nitrogen, and oxygen, together with the elements of group VIII., never occur in a free state in nature, while those of the odd series are very frequently found in that condition; thus, copper[1] (5), silver (7), gold (11), mercury (11), arsenic (5), antimony (7), bismuth (11), sulphur (3), selenium (5), and tellurium (7), frequently occur free;

[1] The numbers in brackets indicate the series to which the elements belong.

Groups.	0	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series.	...	...	...	...	RH_4	RH_3	RH_2	RH_1	...
	...	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8
1		H (1·008)							
2	He (4)	Li (7)	Be (9·1)	B (11)	C (12)	N (14·01)	O (16)	F (19)	
3	Ne (20)	Na (23)	Mg (24·32)	Al (27·1)	Si (28·3)	P (31)	S (32·07)	Cl (35·46)	
4	A (39·9)	K (39·1)	Ca (40·09)	Sc (44·1)	Ti (48·1)	V (51·2)	Cr (52·1)	Mn (54·93)	Fe (55·85) Co (58·97) Ni (58·68)
5	—	Cu (63·57)	Zn (65·37)	Ga (69·9)	Ge (72·5)	As (75)	Se (79·2)	Br (79·92)	
6	Kr (81·8)	Rb (85·45)	Sr (87·62)	Y (89)	Zr (90·6)	Cb (Nb) (93·5)	Mo (96)	—	Ru (101·7) Rh (103) Pd (106·7)
7	—	Ag (107·88)	Cd (112·4)	In (114·8)	Sn (119)	Sb (120·2)	Te (127·5)	I (126·92)	
8	Xe (128)	Cs (132·81)	Ba (137·37)	La (139)	Ce (140·25)	—	—	—	
9	—	—	—	—	—	—	—	—	
10	—	—	—	—	—	Ta (181)	W (184)	—	Os (190·9) Ir (193·1) Pt (195)
11	—	Au (197·2)	Hg (200)	Tl (204·1)	Pb (207·1)	Bi (208)	—	—	
12	—	—	Ra (226·4)	—	Th (232·42)	—	U (238·5)	—	

lead (11), and tin (7), are sometimes so found. On the other hand, chlorine (3), bromine (5), iodine (7), fluorine (2), phosphorus (3), sodium (3), magnesium (3), aluminium (3), and silicon (3), are not found in the uncombined state.

In group VIII. every one of the elements except cobalt is sometimes found in the free state, and the tendency for this to occur appears to increase with the atomic weights of the elements in that group. Further, it may be stated that of the elements of group VIII., only iron, cobalt, and nickel, ever occur in the combined state.

Iron occurs most generally as an oxide, but iron sulphides are also plentiful; cobalt occurs most often as sulphide, and arsenide, but also sometimes as an oxide, while nickel ores are nearly always sulphides, or arsenides, and only very rarely oxides. Mendeléeff differentiated the elements of this group in his second table on account of the ease with which osmium and ruthenium are capable of forming the oxides, OsO_4, and RuO_4, respectively.

He likewise noted many points of similarity between the elements of this group, such as their general grey colour, the great difficulty experienced in fusing these elements, their relatively small atomic volumes, their power of condensing hydrogen, their permeability to that gas, as is well known in the case of platinum, and the double cyanides which they can form with the metals of the alkali group.

Again, the elements of the odd series most often occur

as sulphides, double sulphides, selenides, tellurides, or arsenides, which means that they most readily enter into combination with a negative element also belonging to the odd series. Only in a very few cases are oxides of these elements met with in nature. On the other hand, the elements of the even series usually occur as oxides, or double oxides, that is, as silicates, carbonates, sulphates, aluminates, etc., and in only three cases do they occur as sulphides.

In the odd series, the tendency of members of any particular group to occur in nature as a sulphide increases, while the tendency to occur as an oxide diminishes, with an increase in the atomic weight. Thus in group I. sodium never occurs as a sulphide, but very frequently as a double oxide (silicate), while silver never occurs as an oxide, but very often as a sulphide. Copper, which lies between these two as regards atomic weight, occurs both as an oxide and also as a sulphide. The same is true in group II. for magnesium, cadmium, and zinc, and also for elements similarly placed in groups III. to VI.

The following tables of odd and even series, show clearly the very marked nature of these peculiarities.

Generally speaking, those elements which have the lowest atomic weights in the various groups, differ from the other members in their characteristic properties. Lithium and chlorine are particularly good examples of this; the former, although possessing alkaline properties, is very unlike sodium and potassium in other

Even Series.

	I.	II.	III.	IV.	V.	VI.	VII.	Remarks.
2	Li O	Be O	B O	C O	N O	O S,O		O indicates that the element occurs in nature as an oxide, or double oxide, while S indicates the sulphide as a native form. Oxygen and manganese only very rarely are found as sulphides. There are no exceptions to the rule for oxides.
4	K O	Ca O	Sc O	Ti O	V O	Cr O	Mn S,O	
6	Rb O	Sr O	Y O	Zr O	Nb O	Mo S,O		
8	Cs O	Ba O	La O	Ce O	Di O			
10	—	—	—	Yb O	Ta O	W O		
12	—	—	—	Th O	—	U O		

Odd Series.

	I	II	III	IV	V	VI.	Remarks.
1	H O,S						S indicates that the elements occur in nature as sulphides, selenides, or tellurides; O, as oxides. Sodium, silicon, aluminium, magnesium, and phosphorus never occur as sulphides; lead, antimony, arsenic, and bismuth, only very rarely as oxides.
3	Na O	Mg O	Al O	Si O	P O	S S	
5	Cu O,S	Zn O,S	Ga S	...	As O,S	Se S	
7	Ag S	Cd S	In S	Sn O,S	Sb O,S	Te S	
9	—	—	—	—	—	—	
11	Au (only occurs free)	Hg S	Tl S	Pb O,S	Bi O,S	—	

respects, and fluorine is also very different in some of its properties from the other members of the halogen group. It may be further stated, that lithium, beryllium, boron, carbon, nitrogen, oxygen. fluorine, sodium, magnesium, aluminium, and silicon are all apparent exceptions to the theory of odd and even series, for, although the element sodium belongs to the same sub-group as copper, silver, and gold, it does not resemble those elements in anything like the same degree which they resemble one another, and this is true also with respect to the other elements named, hence the term "Typical Elements" as applied to some of them by Mendeléeff. The letters R_2O, RO, etc., at the top of the table indicate the highest oxides which the elements in any particular group are capable of forming, R of course being used as the general symbol for an element. Some elements such as magnesium, seem capable of forming one oxide only ; but the great majority of elements have the power to form more than one oxide. The oxides of the elements of group I. are generally basic in nature, like Na_2O and Cu_2O. Those of the elements in group II. are also almost exclusively basic, although their basic nature is not so pronounced as in those of group I. As we proceed from group II. to group VII., the oxides of the elements become less and less basic, and their acid properties more and more marked ; until in the case of the elements in group VII. the basic properties are scarcely developed at all. So that those elements like sodium, which occur in group I., at the beginning

of a period, form alkalies, while those in group VII., like chlorine, form acid oxides.

With reference to the elements contained in the same groups, it may be pointed out that oxides of elements belonging to the even series exhibit stronger basic properties than the oxides of elements in the uneven series, in fact the oxides in the latter case are often acid in character. Such are the oxides of phosphorus, arsenic, etc. Speaking very generally, it may be said that acid oxides are most often formed by elements which belong to the uneven series and are of small atomic weights, while the oxides of the elements of greater atomic weight, especially if they are members of an even series, are usually basic in character. The highest oxides of all, R_2O_8 or RO_4 are very rare, in fact only two are known, viz., OsO_4 and RuO_4. In any one series the power to combine with oxygen increases with the atomic weight, and the periodicity of this property is at once apparent by a reference to the table.

The periodic repetition of certain characteristic properties in the elements is well illustrated by the following examples :—

Halogens, Group VII.	Atomic Weights.	Series.	Alkalies, Group I.	Atomic Weights.	Series.
Fluorine (?)	19	2	Sodium (?)	23	3
Chlorine	35·5	3	Potassium	39	4
Bromine	80	5	Rubidium	85	6
Iodine	127	7	Cæsium	133	8

If we represent the typical compounds by the notation RX, RX_2 . . . RX_8 the following generalisations with regard to certain compounds are true. No hydrogen compounds of any element occur of a higher type than RX_4. There are relatively few compounds which are representative of a higher type than RX_3; and lastly, it may be noted that the sum of the number of atoms of hydrogen and oxygen which occur in combination with the elements to form the higher types of compound, is always equal to 8. Thus PH_3, P_2O_5; SH_2, SO_3 (S_2O_6); NH_3, N_2O_5; etc.

The following table will show other examples of this kind, and will also illustrate the periodic nature of the connection which exists between the valency of the elements and their atomic weights, by reference to compounds which the elements form with hydrogen, chlorine, and oxygen. Besides this, it indicates the variations on the valency which occur in some of the elements, and it will be seen that those elements which form compounds of the form RX_n, may also form others which can be represented by RX_{n-2}, or RX_{n-4}. Thus we have SO_2, and SO_3, where sulphur unites with two and three atoms of the element oxygen which itself is divalent. While this is the more general rule, it is also quite possible for even and uneven valencies to be exhibited by one and the same element. $CuCl_2$, Cu_2Cl_2; and $HgCl$, $HgCl_2$ may be quoted as examples of this type.

In the table are given the principal compounds which the elements form with oxygen, chlorine, and hydrogen

(except in the case of carbon). Those which indicate directly the grouping of the elements, by means of the valency which the elements exhibit, are underlined. Those elements in groups V., VI., and VII., are reckoned as possessing two valencies V., III. ; VI., II. ; and VII., I., respectively.

It will be noted that the hydrogen compounds are only formed by the elements of groups IV. to VII. inclusive, if we except the hydride of copper, and the doubtful ones of sodium and potassium. It is of further interest, that it is only the typical elements, and those elements contained in the uneven series, which possess the power to form these compounds. It will be remembered that these hydrogen compounds, (such for example as hydrochloric acid and ammonia), are either volatile, or gaseous substances, and are also of a very active nature. The elements which are able to form hydrides, have also the power to form organo-metallic compounds by uniting with some hydrocarbon radical of the general composition C_nH_{2n+1}. This property is also possessed by elements in the uneven series which are not able to form hydrides, and in these cases the composition of the compound is of a form proper to the group to which the element belongs, thus we have zinc methyl $[Zn(CH_3)_2]$, and mercury methyl $[Hg(CH_3)_2]$. It is only with very great difficulty that the elements belonging to the even series are able to form compounds with hydrocarbon radicals.

Mendeléeff was the first to use the notation which

describes the hydrates of the elements as compounds of the element with hydroxyl (HO). He further noted that the number of hydroxyl groups with which an element can unite to form a definite compound, depends upon the number of hydrogen atoms contained in its hydride, when such a compound exists. Thus, silicon hydride is represented by the formula SiH_4 and its hydrate by $Si(HO)_4$.

A comparison of the atomic weights of the elements contained in the even or odd series of any particular group, will show that the difference between the atomic weights of two consecutive elements is approximately 45. Thus silver (108) – copper (63) = 45. Iodine (127) - bromine (80) = 47, and so on. The typical elements in the same group differ by only 16 in their atomic weights, thus sodium (23) – lithium (7) = 16, and silicon (28) - Carbon (12) = 16. This difference is usually slightly greater than 16 when the elements belong to neighbouring periods of the same group. In the higher groups it is usually about 20 for the difference between the atomic weights of elements in the third and fourth series. With the higher series, or in other words, with elements of higher atomic weights, this difference increases with the atomic weight, until in series 10 to 11, and series 11 to 12, it becomes about 26.

Now, there is a fair amount of regularity in all this, and Mendeléeff was able to turn this to account in what he called the 'atom analogues' of an element. To explain this, suppose four elements to

occupy places in the periodic table corresponding to a, b, c, and d in the diagram, then such elements are the atom analogues of the element occupying place x. If the properties of a, b, c, and d are known, then those of x can be obtained by comparison. The atomic weight of x may also be assumed to be about the average of those of the other four elements. To give an actual illustration of this, take the small section of the table given in the next diagram. Then the average of the atomic weights of the four elements given is 78·65, which is approximately the atomic weight of selenium.

Series.			
Even		a	
Odd			
Even	b	x	c
Odd			
Even		d	

	S (32)	
As (75)	Se	Br (80)
	Te(127·5) ?	

In this manner Mendeléeff found it possible to foretell the characteristic properties of elements which were at that time unknown. The elements gallium (eka-aluminium), scandium (eka-boron), and germanium (eka-silicon), were described by him in this manner; thus for example, the properties of germanium were deduced from the known properties of silicon, tin, zinc, and arsenic. He indicated the elements by

the name given in brackets; the prefix 'eka' being derived from the Sanskrit, and meaning 'one.'

How far he was justified in this prophecy is at once apparent by comparing the properties as predicted by him, with those which have been found by experiment, since the elements then predicted have actually been discovered. This is shown in the following table in which the properties predicted by Mendeléeff are given in the left-hand column, and those experimentally obtained in the right-hand column.

Eka-boron (Predicted by Mendeléeff, 1871).	*Scandium* (Discovered by Nilson, 1879).
Atomic weight 44.	Atomic weight 43·75 (H = 1).
The oxide should be represented by the formula Eb_2O_3, and should possess feebly basic properties.	The oxide of scandium has the composition Sc_2O_3 and is a feeble base.
Should be able to form double salts with the sulphate of potassium, and these salts should not be isomorphous with the alums.	Scandium forms a double sulphate with potassium sulphate, and crystallizes in fine columns.
Eka-aluminium (Predicted by Mendeléeff in 1871).	*Gallium* (Discovered by Lecoq. de Boisbaudran in 1875).
Atomic weight 69 about.	Atomic weight 69·35 (H=1).

Eka-aluminium (*contd.*)	*Gallium* (*contd.*)
Should form an oxide Ea_2O_3, which ought to be soluble in ammonia. The new element will form a chloride which should have the formula $EaCl_3$, and a sulphate $Ea_2(SO_4)_3$.	Oxide of gallium, Ga_2O_3, is partially soluble in ammonia. Gallium forms two chlorides $GaCl_3$, and $GaCl_2$.
It should be capable of forming alums and other compounds similar to those formed by aluminium and Ea_2O_3, like alumina, should have feeble but yet clearly marked acid properties.	Alums are readily formed by gallium, as are also basic salts like those formed by aluminium.
Easily obtained in the metallic state.	Gallium as a metal is easily obtained.
Its density should be 5·9 about.	Density 5·95, but when first discovered owing to impurities its density was thought to be 4·7.
It may possibly be discovered by means of the spectroscope.	Gallium was so discovered in zinc blende.
Should be easily fusible.	Melts at 30° C. about.
The chloride should be volatile.	Gallium chloride is easily fusible and is volatile.

Eka-aluminium (contd.)

Eka-aluminium should not be easily acted on by air, probably not at all.

Gallium (contd.)

Heated to redness in air, gallium is not volatilized, and is only superficially oxidized.

Eka-silicon

(Predicted by Mendeléeff in 1871).

The element should have a dark grey metallic lustre, be very difficult to fuse, and its atomic weight should be about 72.

Its specific gravity should be 5·5 about.

It should form an oxide of composition EsO_2, which will have a density of about 4·7.

The oxide should be of a more strongly acid nature than titanic oxide.

EsF_4 should be volatile, but not gaseous, at ordinary temperatures.

It will form a volatile

Germanium

(Discovered by C. Winkler, 1886).

Germanium is a greyish white, lustrous, and very brittle metal. It melts at 900°, and has an atomic weight of about 72 (71·93 when H=1).

The specific gravity of germanium is 5·469.

There is an oxide GeO_2, and its density is 4·703.

The solution of the oxide in water yields an acid.

GeF_4 is most probably a solid, but is very volatile.

$GeCl_4$ is a colourless

Eka-silicon (contd.)	*Germanium (contd.)*
liquid chloride, $EsCl_4$, which will boil at 90° C. about, and have a specific gravity 1·9.	liquid which boils at 86° C., and has a specific gravity 1·887 at 18° C.

Other properties of these elements were predicted with equal success; sufficient are here given to indicate the very real nature of the connection which exists between the element and its atom analogues. The names by which the elements are now known, were given in honour of the country to which the discoverer in each case owed his birth, thus Nilson was a native of Scandinavia, hence scandium; Lecoq. de Boisbaudran was a Frenchman, hence gallium, and Winkler's home was in Saxony, hence germanium.

The discovery of these three elements which so closely fulfilled the prediction of Mendeléeff, the like of which had never before been attempted, was indeed a triumph for the Periodic Law.

He also used the Periodic Law to correct the atomic weights of some of the elements. The atomic weight of uranium previous to 1869 was considered as 120, but, in order to make it fit in the position assigned to it in the table, its atomic weight had to be changed to 240. The reasons given by Mendeléeff for placing uranium in group VI. series 12, can be used for illustrating the method of attacking such problems.

In the other sub-groups K, Rb, Cs; Ca, Sr, Ba, etc.,

the acid character of the oxides decreases, while the basic character increases, with an increase in the atomic weight; one would therefore expect the oxides of elements of the sub-group Cr, Mo, W, and U, to behave in a similar manner. Now if CrO_3, MoO_3, and WO_3 be the anhydrides of the acids, we do find a decrease in their acid properties as the atomic weight increases, consequently the corresponding oxide of uranium (UO_3) should be only a very weak anhydride, and it should likewise exhibit feeble basic properties if it has a higher atomic weight than tungsten, and belongs to the same sub-group. The oxide of uranium does exhibit these properties. Again, chromium, molybdenum, and tungsten, also form oxides having the general composition RO_2 and R_2O_5 (see Table, pages 110-111), and uranium oxides having the same molecular composition are known. When molybdenum and tungsten are being obtained by reducing MoO_3, and WO_3 respectively, these oxides very often give rise to an intermediate oxide which has a blue colour. The oxide of uranium, UO_3, behaves in a precisely similar manner, for by this means the oxide, known as the "green oxide" of uranium, is produced.

Only one member of the sub-group forms the higher chloride RCl_6, viz. :—tungsten, and the compound in this case is very unstable. There is in each case, however, a lower volatile chloride which is capable of being decomposed by water into a non-volatile compound and the metal. Uranium forms UCl_4, which is a

volatile compound, and is easily decomposed by water. Tungsten has a very high specific gravity (19·0), and that of uranium is also very high (18·7).

Lastly, the higher oxides RO_3, of uranium, chromium, and tungsten, usually have a yellowish tint, while the lower oxides are green, or blue, in colour.

Thus the analogy of uranium to the other elements in sub-group (even series) VI. was apparent, and so it was placed in that group, and its atomic weight altered by Mendeléeff to 240. Zimmerman in 1881, found the vapour density of UBr_4 and UCl_4, and by means of these he was able to confirm the atomic weight of uranium as 240.

Indium may be taken as another example in which the atomic weight was changed in order that the element might fit in with the arrangement according to the Periodic Law. The equivalent of that element was known, but its atomic weight had been a matter of great uncertainty. Now, if the element were monovalent, according to the equivalent experiments its atomic weight should be 37·7, if bivalent $37{\cdot}7 \times 2 = 75{\cdot}4$, and so on. There was no place for an element of atomic weight 75·4 in group II., and since the vapour density, specific heat, and crystallization of its compounds were all unknown, there was just as much reason for consider- it as trivalent, tetravalent, etc. If it proved to be a trivalent element, the composition of its highest oxide would be In_2O_3, and it would fall into position in the table between cadmium and tin. Now, the density of

cadmium is 8·6, that of indium 7·4 and that of tin 7·2. The basic properties of the oxides CdO, In_2O_3, and SnO_2, likewise vary in a regular manner; and, lastly, indium is capable of forming alums, so that we should expect it to belong to group III., and thus occupy the vacant place in series 7 between cadmium and tin. Here it was placed, and later on, when its atomic heat was ascertained, the wisdom of the choice became apparent.

Yttrium was thought to form an oxide having the composition YO, but in 1870 this was corrected by the aid of the periodic table, and a position in group III. was then assigned to that element.

Numerous other changes of this sort were made by Mendeléeff; among these may be mentioned the change of the atomic weight of titanium from 52 to 48, a change which was afterwards confirmed by Professor Thorpe. Lastly, the results of earlier analyses had tended to show that osmium had a greater atomic weight than iridium, and the latter a greater atomic weight than platinum. That order of these elements was however reversed by Mendeléeff, and in this also his prophecy has been proved to be correct.

It will be seen from the table on pages 110-111 that several elements have the power to form peroxides, such as Na_2O_2, BaO_2, etc., and some chemists have been of the opinion, that the existence of such compounds weakens the conclusions of the periodic law, at least, so far as the oxides are concerned. Mendeléeff did not however consider this to be so, for all the peroxides are endowed with

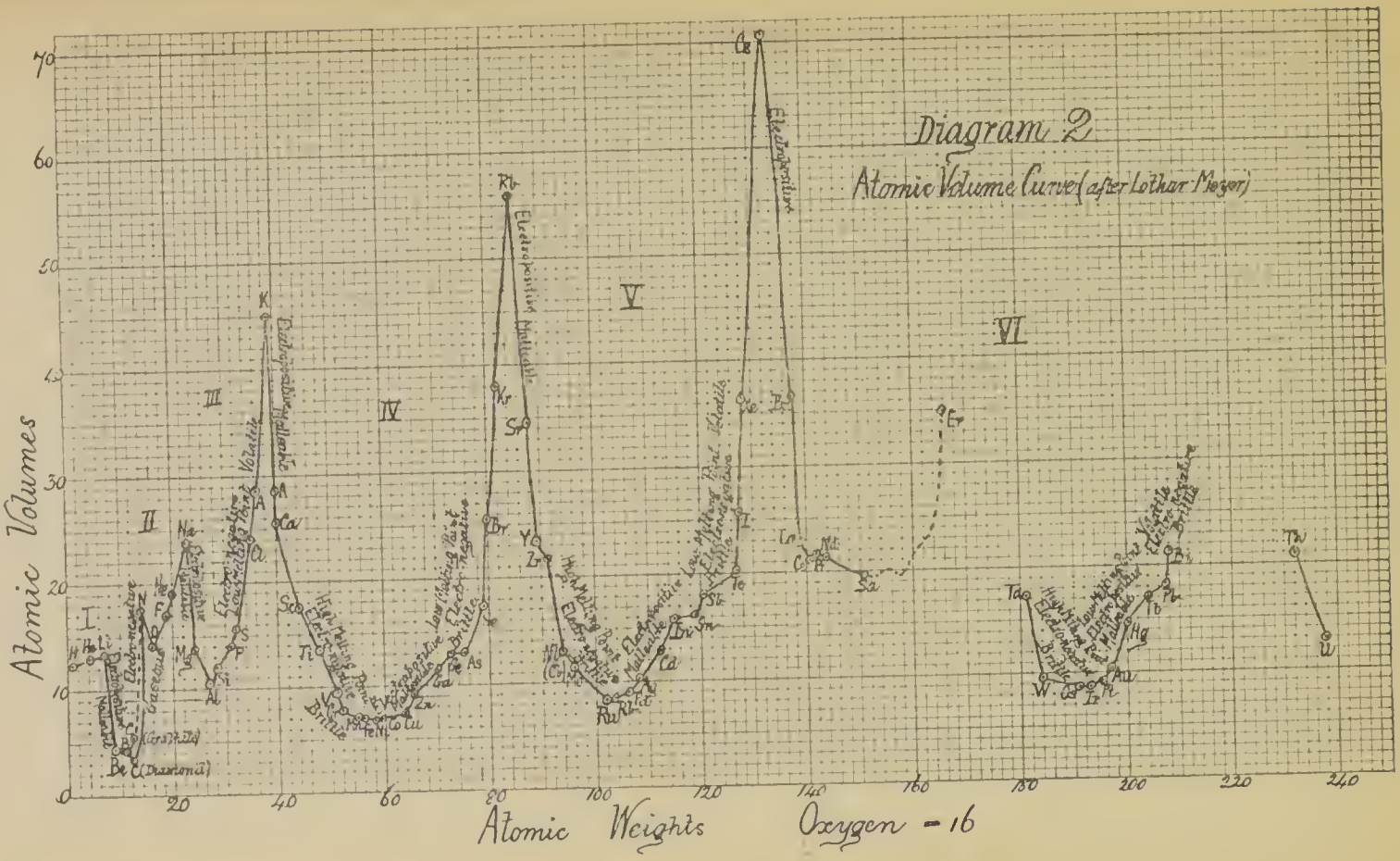


Diagram 2
Atomic Volume Curve (after Lothar Meyer)
Atomic Volumes
Atomic Weights Oxygen = 16
I
II
III
IV
V
VI
0
10
20
30
40
50
60
70
20
40
60
80
100
120
140
160
180
200
220
240

certain properties which are obviously common to all of them, and at the same time distinguish them from the actual salt-forming oxides of the higher types; especially is this so in the ease with which they are decomposed by means of simple contact agencies. They are likewise incapable of forming salts of the common type, and they very readily combine with other peroxides. The power possessed by hydrogen-peroxide H_2O_2 of combining with barium peroxide BaO_2, is an example of this. Again, some groups are especially characterized by their capacity for forming peroxides as is seen by the table.

It forms a pleasant change, to pass from these tabular methods of dealing with the grouping of the elements, to the work of Lothar Meyer, in which by means of the rise, fall, and slope of a curve, he was able to show the periodic variations of many of the chief physical properties of the elements; this we shall now proceed to consider.

Lothar Meyer's Atomic Volume Curve

The work of Lothar Meyer in connection with establishing the theory of the Periodic Law, is second only in importance to that of Mendeléeff. His first attempt in this direction has already been given, but it is by his atomic volume curve that his work on this subject will be best remembered.

The accompanying diagram is a reproduction of that

curve, in which the atomic weights are plotted as abscissæ, and the atomic volumes as ordinates. It has however been brought up to date, and differs slightly in detail of form from that of Meyer. Those elements, the necessary data for which were not known when the original appeared, and the elements of the argon group which had not then been discovered, have been introduced.

The atomic volume of an element is obtained by dividing the atomic weight of the element by its specific gravity, or, in other words, it is the volume in cubic centimetres which the atomic weight expressed in grams would occupy. It will be seen from the diagram, that the elements arrange themselves in six divisions when plotted in this manner. There are four well-marked points in which the curve reaches a maximum; and if we omit the irregularity for nitrogen, and allow the curve to pass through graphite instead of diamond, there is a great similarity in its form between the elements lithium and sodium, and sodium and potassium. The portions between potassium and rubidium, and rubidium and cæsium are likewise very much alike in form. The curve rises regularly from nickel, cobalt, copper, etc., to zinc, gallium and germanium, and then begins to show a tendency to descend, for it becomes much less steep until arsenic is reached. In the next division the same kind of thing is repeated for it rises regularly and rapidly from palladium, silver, etc., towards cadmium and indium, and then again shows a tendency to descend,

for the gradient is much lower toward tin, and then there is a sharp rise to antimony. Where these slight irregularities occur we have elements which behave in a somewhat irregular manner with regard to their other properties; for example, the melting-points of these elements are by no means so regular as those of elements on other parts of the curve; and as might be expected, the same also applies to their co-efficients of expansion.

Not only does this diagram show the manner in which the atomic volume of the elements is a periodic function of their atomic weights, but the periodic nature of many other properties is also demonstrated.

The elements which possess the largest atomic volumes, that is, those which lie on the curve, at, or very near the point at which it rises to a maximum, are those which expand the most when subjected to a rise of temperature; while those situated near the minima have the smallest co-efficients of expansion. Those metallic elements which are characterized by their brittle nature, and high specific gravity, have places on the descending portions of the curve just before the minima are reached; on the other hand, those elements which are brittle but are of a non-metallic nature, are on the ascending portions of the curve.

The more ductile metals occur at the maxima and minima, or immediately follow the elements which are situated at these points. These ductile elements crystallize as a rule in the regular system; while the more brittle elements and those on the ascending portions of

the curve which are more volatile, crystallize in other systems.

With regard to the electro-positive and electro-negative properties of the elements it may be said, that they are possessed in a well-marked degree, only by those which have a comparatively large atomic volume. It appears that the electro-positive or electro-negative character is very largely influenced by the rate of change in the atomic volume from one element to the next, that is, by the slope of the curve. The electro-positive elements which are situated near the maxima, and the volumes of which differ from the volumes of the neighbouring elements by a comparatively large amount, exhibit the electro-positive property in a much greater degree than those situated at another maximum where the difference between the volumes of neighbouring elements is small.

Again, phosphorus, sulphur, chlorine, bromine, selenium, and arsenic, are strongly electro-negative, and there are great differences between their respective atomic volumes, as can be seen by a reference to the curve. There is a less difference between the atomic volumes of tin, antimony, and iodine, and in these the electro-negative property is by no means so clearly marked. Between the atomic volumes of lead and bismuth, the difference is still less, and consequently the electro-negative properties of these elements are still less developed.

With regard to this Meyer says :—" The aggregation of

a large mass in a small space, appears incompatible with the development of either a strongly marked electro-positive, or electro-negative character."

The electro-positive character of the elements, lithium, sodium, potassium, rubidium and cæsium; and beryllium, magnesium, calcium, strontium and barium; increases with ascending atomic weights, so that cæsium is the most electro-positive of the first, and barium of the second set. In the case of boron, aluminium, scandium, yttrium and lanthanum, there is also a gradual increase of electro-positive property with an increase in the atomic weight; and it may be mentioned that an increase of the basic properties takes place at the same time; thus the hydroxide of boron is a weak acid, that of aluminium is also a weak acid, but it likewise acts as a fairly strong base, and so on. Carbon, silicon, and titanium, do not possess such well-defined basic nor electro-positive characters as the elements just considered, for these three, although on a descending portion of the curve, yield acids, still those like zirconium, cerium, and thorium, which have higher atomic weights, do exhibit a more positive nature. Here it may be noted, that those elements, the oxides and hydroxides of which can act as bases, are electro-positive, and those whose oxides, hydroxides, and sometimes even hydrides (as for example HCl), are acids, are electro-negative. Speaking generally it may be said that the elements between lithium and sodium, and also between sodium and potassium, which lie on ascending portions of the curve

are electro-negative, while those on the descending portions are electro-positive. For the fourth, fifth, and sixth divisions of the curve, those elements which occur just after the maxima and minima are electro-positive, while the electro-negative elements will be found just before these points. Fluorine, chlorine, bromine, and iodine, are the most electro-negative of the elements, and all these are situated on ascending portions of the curve just preceding the points at which it reaches a maximum.

Those elements which melt at low temperatures, are situated near the points at which the curve is a maximum, and on ascending branches, while those elements on the lower descending portions of the curve have higher melting-points. The exceptions to this rule are to be found among those elements which are situated at or near those irregularities to which reference has already been made. Among such exceptions are the elements arsenic and selenium, which are near the first-mentioned irregularity ; and tin, antimony, and tellurium near the second. Among those elements of still higher atomic weight, thallium, lead, and bismuth, are exceptions. It is worth noting that, in all these cases the melting-points as obtained by experiment, are too high to fit in with the above rule. Only those elements which can be easily fused, and those which are volatile are to be found on ascending portions of the curve ; the elements on the descending portion and foot of the curve, are those which are less easy to fuse. On the ascending part between carbon and sodium ; nitrogen, oxygen and

fluorine are gases ; in the next ascending part, chlorine is a gas, and both phosphorus and sulphur melt at comparatively low temperatures. In the third ascending portion all the elements after zinc fall in with the above rule. In the next the elements after silver ; and in the last part of the curve mercury represents these volatile elements.

Lastly, those metals which are of a highly magnetic nature, namely iron, nickel, and cobalt, have very small atomic volumes, while the metals which are diamagnetic such as bismuth, have larger atomic volumes. At the same time, both potassium and sodium, which occupy two of the maxima on the curve, are slightly magnetic, while copper and zinc, which are elements having atomic volumes only very slightly larger than that of iron, are slightly diamagnetic. In a general way it may be stated that all the elements situated on the main ascending portions of the curve are diamagnetic, while those on the descending parts and the foot of the ascending are magnetic.

With regard to the periodic table, it is found that in the case of a large number of elements, those which belong to the even series are magnetic, while those which belong to the odd are diamagnetic ; and that for those elements belonging to the same group, the diamagnetism increases with an increase of atomic weight. The following table will illustrate these points. The positive sign indicates magnetic, and the negative sign indicates diamagnetic properties.

Series.	Element.	Magnetic Property.	Observer.
1	Hydrogen	+0·008 V	G. Quincke, *Wied. Ann.* 34, 401, 1888.
2	Beryllium	+0·79 M, V	St Meyer, *Wied. Ann.* 68, 325, 1899.
2	Boron	+4·3 M, V	,, ,, ,,
2	Carbon (Graphite)	+2·0	J. Königsberger, *Wied. Ann.* 66, 698, 1898.
	Carbon (Diamond)	−1·14 V	St Meyer, ,, 68, 325, 1899.
2	Oxygen	+0·129 V	G. Quincke, ,, 34, 401, 1888.
2	Nitrogen	+0·001 V	,, ,, ,,
3	Sodium	+2·2	J. Königsberger, ,, 66, 698, 1898.
3	Magnesium	+4·0	,, ,, ,,
3	Aluminium	+1·88	A. P. Wills, *Phil. Mag.* [5], 45, 432, 1898.
3	Silicon	+0·2 M, V	St Meyer, *Wied. Ann.* 68, 325, 1899.
3	Phosphorus	−1·6	G. Quincke, *Wied. Ann.* 24, 347, 1885.
3	Sulphur	−0·77	A. P. Wills, *Phil. Mag.* [5] 45, 432, 1898.
4	Potassium	+3·6	J. Königsberger, *Wied. Ann.* 66, 698, 1898.
5	Copper	−0·82	,, ,, ,,
5	Zinc	−0·96	,, ,, ,,
5	Selenium	−0·50	,, ,, ,,
5	Bromine	−1·4	G. Quincke, ,, 24, 347, 1885.
6	Palladium	+60	J. Königsberger, ,, 66, 698, 1898.
7	Silver	−1·51	,, ,, ,,
7	Antimony	−3·75	L. Lombardi, *Mem. R. Acc. Torino* [2], 47, 1, 1897.
7	Tellurium	−2·10	J. Königsberger, *Wied. Ann.* 66, 698, 1898.
7	Iodine	−0·39 M, V	P. Curie, C.R. 116, 136, 1893.
8	Platinum	+29·0	J. Königsberger, *Wied. Ann.* 66, 698, 1898.
11	Gold	−3·07	,, ,, ,,
11	Mercury	−2·6	G. Quincke, ,, 24, 347, 1885.
11	Lead	−1·37	J. Königsberger, *Wied. Ann.* 66, 698, 1898.
11	Bismuth	−13·3 V	L. Lombardi, *Mem. R. Acc. Torino* [2], 47, 1, 1897.

The figures given in the table represent the magnetic susceptibility of unit mass, or unit volume, of the element multiplied by 10^6, M indicates those for which the unit mass has been taken. The susceptibility of air is taken as equal to zero, except in those cases in which V occurs, when the susceptibility of a vacuum is taken as zero. It will be seen that the elements of the third series are in the main paramagnetic, but the series ends with a diamagnetic substance; the only other exception to the rule for odd and even series occurs in series two, and is the diamond, which is diamagnetic, but this is counterbalanced by graphite, which is much more strongly paramagnetic. To illustrate the second point the following illustrations will suffice :—

Series.		Series.	
3	Sodium +2·2	3	Phosphorus — 1·6
5	Copper —0·82		...
7	Silver —1·51	7	Antimony — 3·75
11	Gold —3·07	11	Bismuth —13·3

In the first column, sodium is paramagnetic, but with an increase of atomic weight copper is slightly diamagnetic, and then onwards there is an increase in that property until gold is reached. In the second column there is a gradual increase in diamagnetic properties throughout, with increase of atomic weight.

Several other interesting points can be observed by a

elose study of the positions of the elements on this curve. Perhaps one of the most notieeable, eentres round the elements belonging to group V. of Mendeléeff's table, whieh elements form pentoxides. Of these, vanadium, niobium, and tantalum, are on the lower descending portions of the eurve, while nitrogen, phosphorus, arsenic, antimony, and bismuth, are on the lower ascending parts. So far as their pentoxides are coneerned, the following points with respeet to their stability, and the ease or otherwise with which they ean be reduced are worth noting. Nitrogen pentoxide (N_2O_5), has no great stability, and melts at a very low temperature; phosphorus pentoxide (P_2O_5) sublimes at red heat, and ean be entirely deeomposed by heating it with carbon; vanadium pentoxide (V_2O_5) ean be easily redueed by using hydrogen or earbon, and melts at a high temperature without undergoing decomposition; arsenic pentoxide (As_2O_5) ean be reduced to As_2O_3 by the aetion of heat alone; and antimony pentoxide (Sb_2O_5), and bismuth pentoxide (Bi_2O_5), ean also be reduced in a similar manner; the latter losing oxygen at 150° C. On the other hand, niobium pentoxide (Nb_2O_5), and tantalum pentoxide (Ta_2O_5), ean neither be readily melted, nor do they volatilize. They are not deeomposed, even when they are heated until white heat. Niobium pentoxide can however be reduced by heating with hydrogen, but tantalum pentoxide ean only be reduced by heating with charcoal, and even then only at very high temperatures. These two elements which form the most stable and

least easily reducible pentoxides, also form pentachlorides ($NbCl_5$ and $TaCl_5$) which can exist as gases, while the pentachlorides of both phosphorus and antimony split up so as to form the trichloride and free chlorine, when they are heated. Several interesting facts may be noted with respect to these elements themselves. Thus, nitrogen is on an ascending branch, on which all the elements are gaseous ; it is also followed by electro-negative elements, and as can be seen by the curve there is no great difference between the atomic volume of nitrogen and that of its neighbours.

Phosphorus occupies a similar position to nitrogen, but nitrogen is slightly further from the minimum ; and that element (P) is followed by sulphur, which has a low melting-point, and then the remaining elements on the ascending branch are gaseous. Arsenic and antimony occupy similar positions on the curve, following immediately after electro-positive elements, and both are followed by elements of low melting-point, which are also volatile elements.

Bismuth may be looked upon as completely hemmed in by electro-positive elements, for it is not followed by electro-negative elements as is the case with each of the other members of this group. Of the three on descending portions of the curve, vanadium lies nearest a minimum, and is also closer to a group of electro-positive elements than the other two.

The curve has been made as complete as possible. Helium, neon, argon, krypton, and xenon have been

placed in position according to their accepted atomic volumes, but argon has been placed in two positions. The position of that element on the descending branch fits in best with its accepted atomic weight, but its analogy to the other inert gases would make it appear that its place ought to be on the ascending branch.

It will be seen that the uniformity of the curve requires a higher atomic weight for iodine than for tellurium, and that it does not matter whether cobalt precedes nickel, or *vice versâ*, as the curve is irregular in that portion. Some of the more marked periodic variations have been shown on the curve itself, in order that by an examination of the diagram alone, they may become fixed upon the mind of the reader.

CHAPTER V

THE WORK OF CARNELLEY

The first English chemist to work out in detail the manner in which the properties of the elements are periodic functions of their atomic weights, was Carnelley. His papers on this subject appeared in the *Philosophical Magazine* between the years 1879 and 1885. They are chiefly of interest on account of his extensive researches, firstly, those connected with his earlier work on the melting- and boiling-points of the halogen compounds of the elements, and, in the second place, those carried out later on, for the purpose of the extension which he made so as to bring the metallo-organic compounds to his aid in defence of the periodic theory. In one of his first papers he considered the melting-points of the elements themselves, and he pointed out, that just as the atomic weights of the middle member of a triad is the mean between those of the extreme members, so is its specific gravity, its melting- and boiling-points, if reckoned from the absolute zero of temperature, and also the heat evolved by it when uniting with hydrogen.

The well-known chlorine group can be used to illustrate this point as follows :—

Element.	Atomic Weight.	Specific Gravity.	Melting-Point (Absolute).	Boiling-Point (Absolute).	Heat evolved by union with one atom of hydrogen.
Chlorine . .	35·45	1·33 at 15° C.	171	240	23,783
Iodine . .	126·97	4·66 at 15° C.	387	447	−3,606
$\frac{\text{Chlorine} + \text{Iodine}}{2}$	81·21	2·99	279	343	10,088
Bromine . .	79·96	2·99 at 15° C.	266	336	9,322

The figures obtained by taking the mean between the values for chlorine and iodine are in all cases except the specific gravity (it was so, in this case also, in Carnelley's paper, since he used the specific gravity of iodine at 107° C., viz. 4·00, instead of the one used in the table) considerably different from the experimental results, yet in every case they are of the same order of magnitude. The melting-points of the elements are given in the following table in which the elements are arranged according to Mendeléeff's Periodic Law. A complete list has been given, and by its aid, together with the diagram in which the atomic weights of the elements are plotted as abscissæ, and their melting-points (absolute) as ordinates, many important points are demonstrated. Omitting the elements of the zero group, all of which have low melting-points, and considering the other elements as divided into odd and even series, it will at once be noticed that a gradual increase in the temperature of the melting-points occurs in series 2, from lithium (453°) to carbon (not known), then a very sudden fall to nitrogen (62°), and a con-

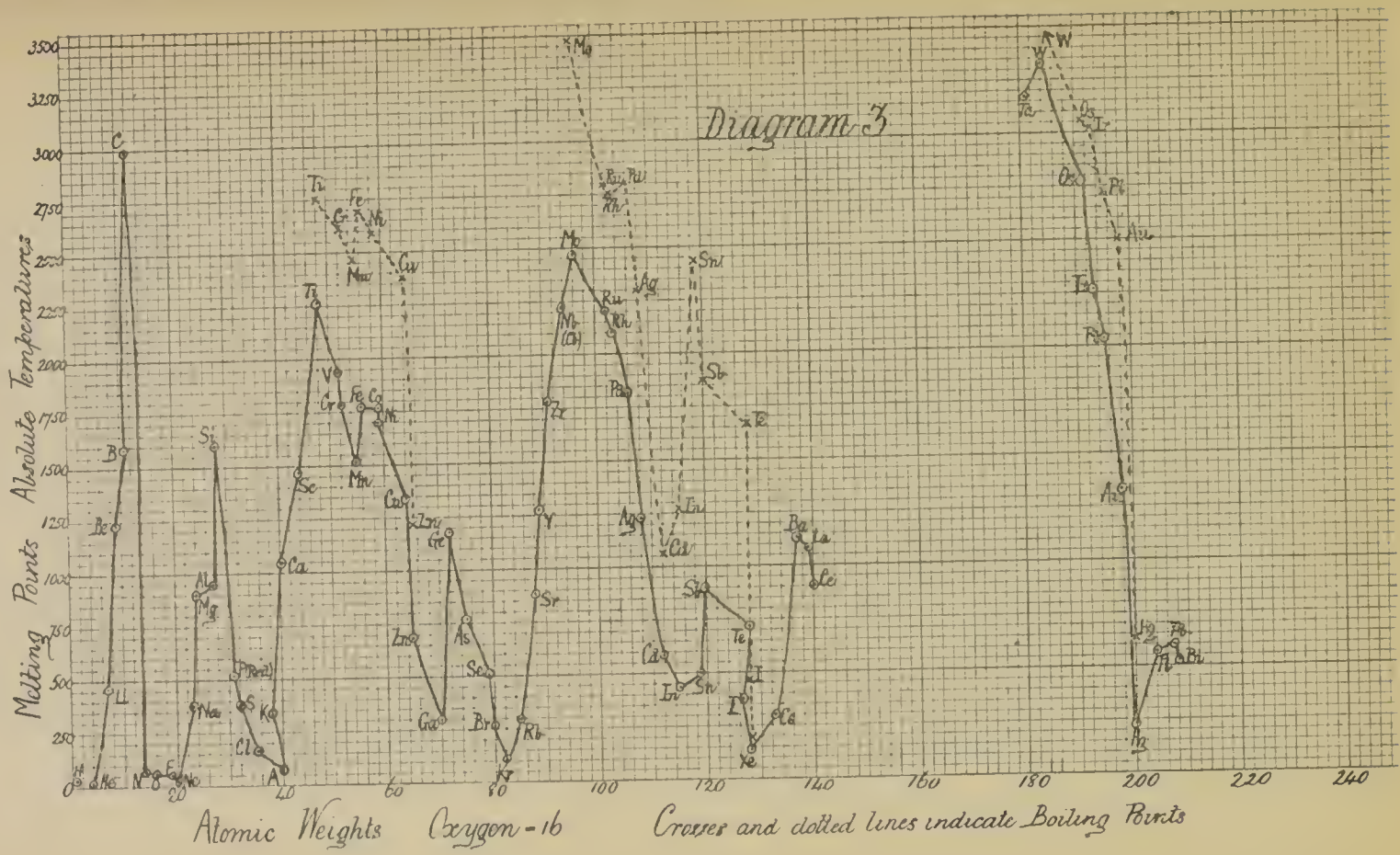


Diagram 3
Melting Points Absolute Temperatures
Atomic Weights Oxygen = 16
Crosses and dotted lines indicate Boiling Points

tinuance of low values to the end of the series. The same kind of relationship exists among the elements of series 3, first a rise from sodium (370°) to silicon (1700° about), then a sudden drop to phosphorus (317°), and a series of low temperatures to the end. Thus there is a clearly marked periodic change in the absolute temperatures of the melting-points of the elements of these two series. With the long periods of two series each, there is at first in the even series a rise of temperature with an increase of atomic weight, then a gradual and slight fall; in the odd series a decrease at first takes place as the atomic weights increase, then a sudden increase occurs, and lastly another decrease. Thus, in the even series, potassium melts at 335°, titanium at (?) 2273, vanadium at 1953°, and nickel at 1708°, or it can be better shown by including the elements to manganese (1518°) only; while in the odd series, copper melts at 1357°, gallium at 303°, then germanium at 1173°, and lastly bromine at 266°.

The same periodic rise and fall appears in the elements of series 6 and 7, and so on for the remainder of the table. The analogous elements of the eighth group, the atomic weights of which are so nearly equal for elements of the same series, are also characterised by having melting-points which differ only slightly from one another.

It is interesting to note, however, that if nickel is assumed to have a higher atomic weight than cobalt, there is then in all three cases a gradual fall in the

temperature at which these elements melt as their atomic weights increase.

In the case of the elements of the zero group, the melting-point temperatures gradually rise as we proceed from helium (4°) to xenon (133°). All these variations are indicated in the table and accompanying diagram. Sufficient boiling-points for the metals have been inserted on the diagram to make clear the periodic variation of these also.

Since the temperatures of the melting- and boiling-points of the elements are periodic functions of their atomic weights, it follows that the latent heat of vaporisation of the gram molecule of the element is also a periodic function; for it has been shown by Trouton that the latent heat of vaporisation of a gram molecule of an element at constant atmospheric pressure is 23 T calories, where T is the temperature of its boiling-point. Richards[1] has recently shown that this is also true for the total quantity of heat in the vapour of an element at its normal boiling-point. To do this he assumes that Dulong and Petit's constant becomes 6 at absolute zero, and 10 at the melting-points of the metals; thus the mean value of the atomic heat between absolute zero and the melting-point of the metal is 8, and so, if the temperature of melting-point is 't,' the total quantity of heat contained in the metal at its melting-point is 8t calories. It is also known that the latent heat of fusion for a metal can be represented by 2t, so that

[1] *American Electro.-Chem. Soc. Trans.*, xiii. pp. 447-451, 1908.

the molten liquid will contain $8t+2t=10t$ calories. The specific heat of liquid metals is practically the same as that of the metals themselves at their melting-point, so that the heat required to raise the liquid from melting-point (t), to boiling-point (T), is therefore $10(T-t)$ calories, and the total quantity of heat in the liquid at its boiling-point is $10(T-t)+10t$, that is, 10T calories; and again, the total quantity of heat in the vapour at the normal boiling-point must be $23T+10T=33T$ calories. Hence if T is a periodic function so is this quantity.

For the purpose of finding the melting- and boiling-points of their halogen compounds, Carnelley carried out a very extensive series of researches, and from the results he obtained was able to point out the following relationships between the elements.

The melting-points, boiling-points, and heats of formation of the normal halogen compounds of the elements, are a periodic function of the atomic weights of the constituent elements.[1] (By normal chlorides is to be understood such compounds as LiCl, $BaCl_2$, BCl_3, CCl_4, NCl_3, OCl_2 and ICl for the groups I. to VII. respectively.) He stated further, that when the elements are arranged in order of their atomic weights, it is found that the temperatures of the melting- and boiling-points, and likewise the heats of formation of their halogen com-

[1] The question so far as it concerns the heat of formation of the chlorides is again considered in a later chapter. The figures and relations here given are those of Carnelley.

Table of Melting-Points of the Elements.

Temperatures in Degrees from Absolute Zero.

Series.	0	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	...	16·5 H	...	...	...	...	...	...	...
2	He 4	Li 453	Be 1235	B 1573	C 2973	N 62·5	O 50	F 50	...
3	23 Ne	370 Na	906 Mg	928 Al	abt. 1700 Si	V. 317 } P R. 528 } P	388 S	171 Cl	...
4	A 85	K 335	Ca 1053	Sc (?) 1473	Ti (?) 2273	V 1953	Cr 1788 (1762 W.B.)	Mn 1518 (1480 W.B.)	Fe 1776 (1778 W.B.), Co 1773 (1737 W.B.), Ni 1700 (1708 W.B.)
5	—	1353 Cu (1357 W.B.)	692 Zn	303 Ga	abt. 1173 Ge	773 As	490 Se	266 Br	...
6	Kr 104	Rb 311	Sr (?) 873 1073 (?)	Y (?) 1273	Zr 1773	Nb 2223 (?)	Mo 2473	—	abt. Ru 2200, abt. Rh 2180, Pd 1820
7	—	1241 Ag	594 Cd	428 In	505 Sn	902 Sb. (903·5 W.B.)	725 Te	386 I	.
8	Xe 133	Cs 300	Ba 1123	La 1083	Ce 896	...	...	...	...
9	—	—	—	—	—	—	—	—	...
10	—	—	—	—	—	Ta 3183 (?)	W 3353 (?)	...	Os 2773, Ir. 2273, Pt 2026
11	—	1335 Au	234 Hg	577 Tl	600 Pb	543 Bi	...	...	...
12	—	—	Ra (?)	—	Th (?)	—	U (?)	...	...

W.B. *indicates Washington Bureau of Standards.*

pounds, rise and fall periodically nine times, and that the periods so formed correspond precisely with those of the elements in Mendeléeff's table. The maxima occur at the positive ends of the series, and the minima at the negative ends. This may be taken as the general rule, but there are exceptions. These occur among the compounds formed with those elements which occupy the maxima and minima positions on the atomic volume curve, that is with the metals of the alkalies, and carbon, silicon, etc., etc.

When exceptions are found among the elements of group IV. the melting- and boiling-points are lower than that required by the rule, when they are members of the odd series, but higher when they belong to the even series. These instances form no exceptions to the periodic rule, for, as Carnelley pointed out, they themselves vary periodically. With reference to the part played by the halogens themselves, he pointed out that their influence on the temperature depends upon the number of atoms which are contained in a molecule of the compound. Thus, for example, IBr boils at 390°, while ICl boils at 373°, therefore the difference is 17° between the boiling-points of these two compounds; $SbBr_3$ boils at 549°, and $SbCl_3$ at 496°, the difference in this case being 53°; again $SnBr_4$ boils at a temperature 86° higher than $SnCl_4$.

From illustrations of this kind we learn that the greater the number of atoms of the halogen which enters into the compound, the greater the difference between

the boiling-points of the various halogen compounds of the same element. Should one of the elements in a normal halogen compound be changed, then the melting-point of the compound will change also; an increase occurs in the temperature when there is an increase in the atomic weight owing to the change. Thus :—

$SbBr_3$ melts at 363° . . . Atomic weight of Sb 120·2.
$AsBr_3$ melts at 295° . . . Atomic weight of As 75.

An increase of 68° by changing from As to Sb.

Again—

SbI_3 melts at 438° . . . Atomic weight of I 126·97.
$SbBr_3$ melts at 363° . . . Atomic weight of Br 79·96.

An increase of 75° by changing from Br to I.

Further, if we are considering the elements belonging to the same group, then the amount of increase in the temperature at which the halogen compounds melt, when, as for example, iodine is substituted for bromine, depends upon the atomic weights of the elements with which it is united.

Thus AsI_3 melts at 419°, while
$AsBr_3$ melts at 295°, a difference of

124°, which is much greater than occurs with the compounds of iodine and bromine when antimony is substituted for arsenic, as is shown

above. So that the greater change in temperature takes place with the element of smaller atomic weight, and this is the general rule. This is also true when it is the halogens which are changed, and not the other elements, for we have—

$SnBr_4$ melts at 303°, and
$SiBr_4$ melts at 260°, a difference of 43°;
while SnI_4 melts at 419°, and
SiI_4 melts at 393°, a difference of only 26°.

When the atomic weights of chlorine (35·45), bromine (79·96), and iodine (126·97) are compared, it is seen that bromine is nearer to chlorine in atomic weight than it is to iodine; the difference between the first two being 44·51, while it is 47·10 for the two last. Carnelley pointed out that the melting-points, boiling-points, and heats of formation of the bromides are always nearer to those of the corresponding chloride, than to those of the iodide.

Thus the melting-point of NaCl is 1045°,
and the melting-point of NaBr is 981°, a difference of 64°;
while the melting-point of NaI is 901°, a difference of 80°.

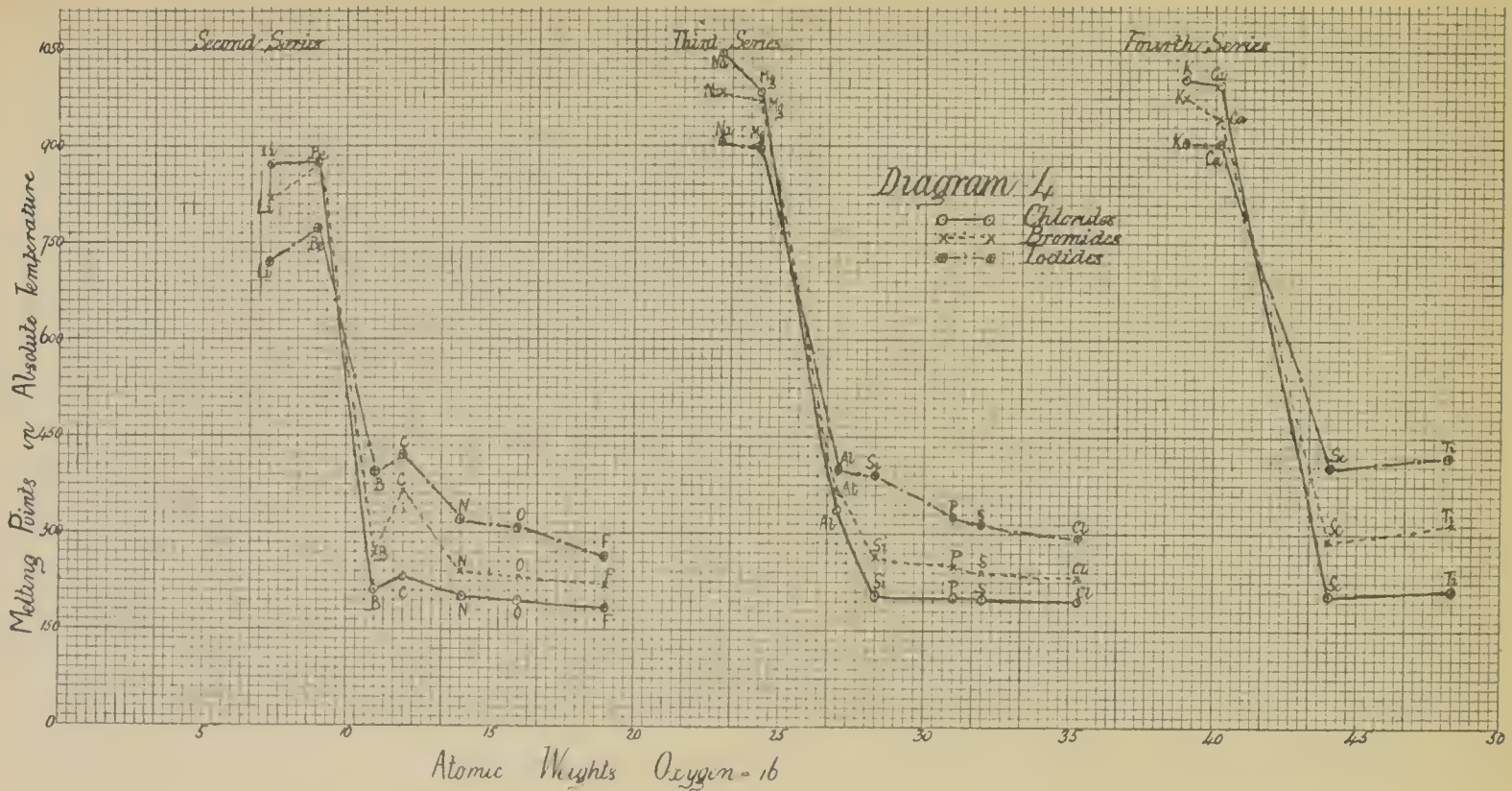
A similar variation to that which has been explained for the halogen compounds, is shown also by the other groups of triads, for it is invariably the case that the atomic weight of the middle member of the group is nearer that of one of the outer members than it is the

Temperatures of Melting- and Boiling-Points of the Halogen Compounds

In Degrees from Absolute Zero.

Series.	Elements.	Chlorides.			Bromides.			Iodides.		
		Melting-Points.	Boiling-Points.	Heat of Formation.	Melting-Points.	Boiling-Points.	Heat of Formation.	Melting-Points.	Boiling-Points.	Heat of Fomation.
2	Lithium	876	...	94,000	820	...	...	719	...	...
	Beryllium	874	...	...	874	...	...	771	...	...
	Boron	210	290	36,166	271	363	24,366	397	493	...
	Carbon	231	351	...	364(?)	462	...	420	620	...
	Nitrogen	200	344	...	244	439	...	322	585	...
	Oxygen	199	251	...	237	346	...	310	465	...
	Fluorine	189	215	...	218	270	...	264	359	...
3	Sodium	1045	...	97,700	981	...	90,600	901	...	74,100
	Magnesium	981	...	75,500	971	...	70,000	896	...	54,000
	Aluminium	340	453	52,000	366	533	42,830	398	623	27,870
	Silicon	205	331	39,400	260	426	30,100	393	563	14,000
	Phosphorus	200	351	25,266	252	444	18,200	328	575	8,900
	Sulphur	199	337	...	240	406	...	315	528	..
	Chlorine	198	240	...	229	286	...	298	373	...
4	Potassium	1007	...	104,600	972	...	99,000	907	...	85,200
	Calcium	992	...	84,800	949	..	75,600	904	...	59,100
	Scandium	236	334	...	293	407	...	404	528	...
	Titanium	246	408	...	312	503	...	423	633	...

The figures in this table are as given by Carnelley.


Second Series
Third Series
Fourth Series
Diagram 4
Chlorides
Bromides
Iodides
Melting Points on Absolute Temperature
Atomic Weights Oxygen = 16
0
150
300
450
600
750
900
5
10
15
20
25
30
35
40
45
50

other. Thus in the triad phosphorus (31), arsenic (75), antimony (120·2), the difference between the atomic weight of the middle element and that of the first is 44; while between the atomic weight of the middle element and that of the last there is a difference of 45·2. Now the boiling-point of PCl_3 is 351°, and

the boiling-point of $AsCl_3$ is 405°, a difference of 54°; while the boiling-point of $SbCl_3$ is 496°, a difference of 91°. The effect which the number of atoms contained in the compound molecule (due to the valency of the element) has, upon the temperature at which these halogen compounds melt or boil, and also upon the heat of formation of these compounds, can be recognized if we examine the elements in the ascending order of their atomic weights. This is shown in the preceding table for the elements between lithium and titanium inclusive; the diagram shows the same for the melting-points of chlorides, bromides and iodides, and the periodic rise and fall of these temperatures with increasing atomic weight is clearly seen.

From this table and diagram it appears that the values for the elements of groups I. and II. in the same series are very nearly the same, while there is a large drop between the second and third members of the series, then a very gradual decrease for the remainder of the series, although the compounds of carbon and titanium, elements belonging to the even series of group IV., have temperatures rather too high, and therefore must be looked upon as exceptions to this rule. It is found

also, that the melting- and boiling-points of the halogen compounds are highest in the case of the iodides, and lowest for the chlorides of the elements belonging to the higher groups (3rd to 7th inclusive).

For those contained in the even series of the first two groups the opposite relation holds true, as it does also for the elements sodium and magnesium. The heat of formation is greatest for the chlorides, and least for the iodides, in all cases. These points are illustrated in the preceding table and diagram, for it will be seen that the line connecting the melting-points of the iodides crosses the other lines after the second element in each series; and the chloride line is similarly crossed by the bromide line.

The effect which the atomic weight of the element united with the halogen has upon the boiling-point of the compound so formed, depends upon the group to which that element belongs.

The melting- and boiling-points of the halogen compounds of the elements of groups I., II., and IV. are given below, and from these it can be seen, that if the elements are considered according to the series to which they belong, then in group IV., the temperatures of the melting- and boiling-points increase with an increase of the atomic weight of the elements for both odd and even series. This is true also for all the groups from the third to the seventh inclusive. For group II. there is also an increase for the elements belonging to the even series. So far as the members of the odd series of the

Melting- and Boiling-Points of Halogen Compounds of Elements in Groups I., II. and IV.

(Members of the Odd Series are in Italics. Temperatures from Abs. Zero.)

	Chlorides.		Bromides.		Iodides.	
	Melting-Points.	Boiling-Points.	Melting-Points.	Boiling-Points	Melting-Points.	Boiling-Points.
Group I.						
Lithium . .	870	...	820	...	719	...
Sodium . .	1045	...	981	...	901	...
Potassium .	1007	...	972	...	907	...
Copper . .	707	abt. 1273	777	abt. 1173	874	abt. 1040
Rubidium .	983	...	956	...	915	...
Silver . . .	724	...	700	...	800	...
Cæsium . .	904	...	...	...	891	...
Group II.						
Beryllium .	874	...	874	..	771	863
Magnesium .	981	...	971	...	896	...
Calcium . .	992	...	949	abt. 1083	904	abt. 988
Zinc . . .	535	953	667	972	719	...
Strontium .	1098	...	903	...	780	...
Cadmium .	814	abt. 1173	844	1083	677	abt. 988
Barium . .	abt. 1181	...	1085	...	(?)	...
Mercury . .	561	576	517	592	514	622
Group IV.						
Carbon . .	231	351	364	462	120	620
Silicon . .	205	331	260	426	393	563
Titanium . .	246	408	312	503	423	633
Germanium .	218	339	271	428	399	565
Zirconium .	326	495	367	555	455	681
Tin . . .	251	389	303	474	419	569
Cerium . .	409	556	434	611	515	735
Lead . . .	338	498	372	555	498	659

first two groups are concerned, their melting-points decrease in value as the atomic weights of the elements increase, while for the even members of the first group there is an increase from lithium to potassium, and then a decrease to cæsium. A more detailed analysis of the figures given in the tables will reveal other facts, such as—the differences between the boiling-points of the different halogen compounds of the same element are greater than the differences between the corresponding melting-points. For example—

The boiling-point of $SnCl_4$ is 389, and

The boiling-point of $SnBr_4$ is 474, a difference of 85°;

While the melting-point of $SnCl_4$ is 254, and

The melting-point of $SnBr_4$ is 303, a difference of only 49°. Even these differences appear to undergo changes of a periodic nature, increasing algebraically from the first to the fourth member of each series, and then diminishing to the last member; and again the differences between the melting-points, boiling-points, and heats of formation of bromide and chloride of any element, are less than between those of its iodide and bromide, and these in turn are less than the differences between the values obtained for the same constants in the case of the iodide and chloride. These and many other relations of a similar kind were pointed out by Carnelley and applied to no less than 3248 cases of which only 180 were exceptions; and of these 73 were due to the following eight substances: CBr_4 and $AlCl_3$, in which the melting-points are too high; $SrBr_2$, SrI^2,

and PI_3 with melting-points too low; AsI_3 with boiling-point too high, and SnI_4, and PI_3 with boiling-points too low. He calculated the probable melting- and boiling-points of a large number of these compounds, making use of the method of limits, and applying the relations which he had found to exist between these compounds. By this means, although it was not possible to actually fix the exact temperature at which the melting or boiling of any halogen compound would take place, he was able to obtain the limits between which those points would be found.

In 1885 he published [1] an account of his researches on the boiling-points and specific gravities of the metallo-organic compounds of the elements as regarded from the point of view of the Periodic Law. Here, again, he found that when the elements are arranged in the ascending order of their atomic weights the temperature of the boiling-points of their compounds formed by union with certain hydrocarbons [he investigated compounds of the elements with CH_3 (methides), C_2H_5 (ethides), C_3H_7 (propides), C_4H_9 (butides), and C_6H_5 (phenides)] rises and falls periodically. The specific gravity of these compounds also shows a periodic variation, diminishing from the beginning to the middle of each series, and then increasing to the end. This is shown in the accompanying diagram. Where exceptions to the general rule as to boiling-points occur, it will be seen that the elements concerned are those

[1] *Phil. Mag.* [5], 20, pp. 259 and 497 *et seq.*

situated either near a maximum or minimum point of L. Meyer's curve. It will also be noticed for any particular element that the temperature of the boiling-point increases, and the value of the specific gravity of the compound diminishes, with an increase in the molecular weight of the organic radical. Thus—

Zinc Methide	boils at	319°.	and has specific gravity	1·386
Zinc Ethide	,,	391°,	,, ,,	1·182
Zinc Propide	,,	432°,	,, ,,	1·098
Zinc Butide	,,	461°,	,, ,,	——

Or,

Mercury Methide	boils at	367°,	and has specific gravity	3·069
Mercury Ethide	,,	432°,	,, ,,	2·444
Mercury Propide	,,	464°,	,, ,,	2·124
Mercury Butide	,,	479°,	,, ,,	1·835

Comparing elements taken from the same group, we find that both the temperature of the boiling-point of the compound formed with the organic radical, and also its specific gravity, increases with an increase in the atomic weight of the element.

Thus in group IV. we have—

	Atomic Weight.	Boiling-Point of Ethide.	Specific Gravity of Ethide.
Silicon . .	28·4	425	0·766
Tin . .	119·0	454	1·187
Lead . .	206·9	473	1·585

Many other relationships with reference to the differences to be observed between the boiling-points of the various

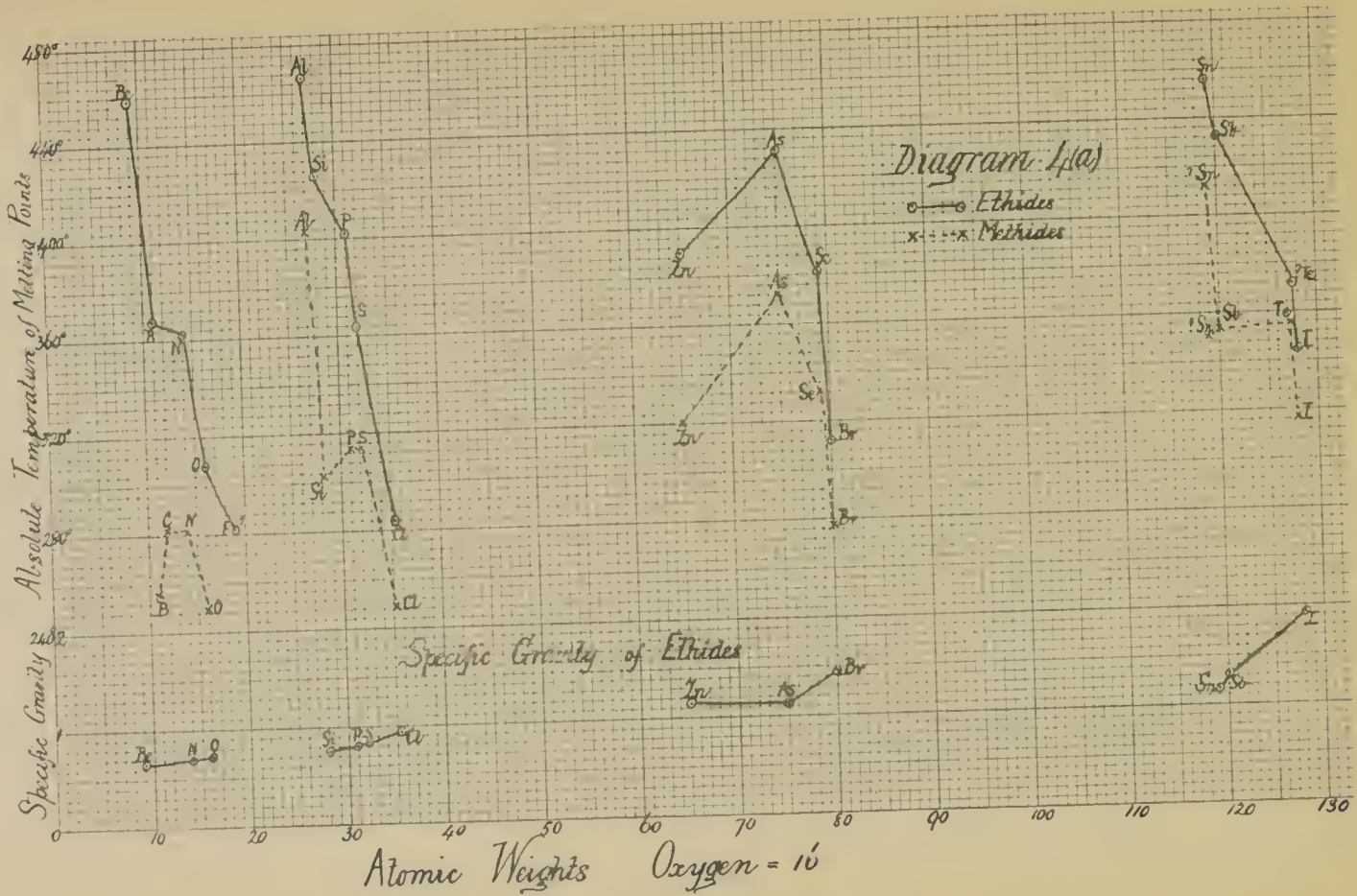


Diagram 4(a)
Ethides
Methides
Specific Gravity of Ethides
Specific Gravity Absolute Temperature of Melting Points
Atomic Weights Oxygen = 16
0
10
20
30
40
50
60
70
80
90
100
110
120
130

metallo-organic compounds, etc., were pointed out by Carnelley; but sufficient have been given to show that in the case of the boiling-points and specific gravities of the compounds of the elements formed with certain organic radicals, there is a periodic variation which is a function of the atomic weight of the element. This work did much towards establishing the Periodic Law on a firm basis; and the laborious work carried out by Carnelley to bring this about entitles him to a foremost place among those, who, either by their own experimental researches, or the consideration of the data obtained by others, have produced what is recognized as a most natural, and at the same time extremely useful grouping of the elements.

CHAPTER VI

OTHER METHODS OF ARRANGING THE ELEMENTS

Since the table due to Mendeléeff first appeared in its present form, other attempts have been made to illustrate the periodicity of their properties by suitable arrangements of the elements.

In 1887 Sir William Crookes contributed some papers [1] dealing with the "Genesis of the Elements," and as the outcome of his work in this direction, he produced a scheme which, while illustrating the development of the elements as he then conceived it, at the same time made clear the periodic relation between the properties of the elements when they are considered in the order of their atomic weights.

Just as the hypothesis put forward by Prout presupposed some common origin for all the elements (and this hypothesis is most decidedly strengthened by the Periodic Law), so, Sir W. Crookes imagined that all the elements were probably evolved from one sole kind of matter, which he proposed to name "protyle." This protyle was not to be considered as matter, such as we know it, but a something, out of which all kinds

[1] *Chemical News*, February and March 1887.

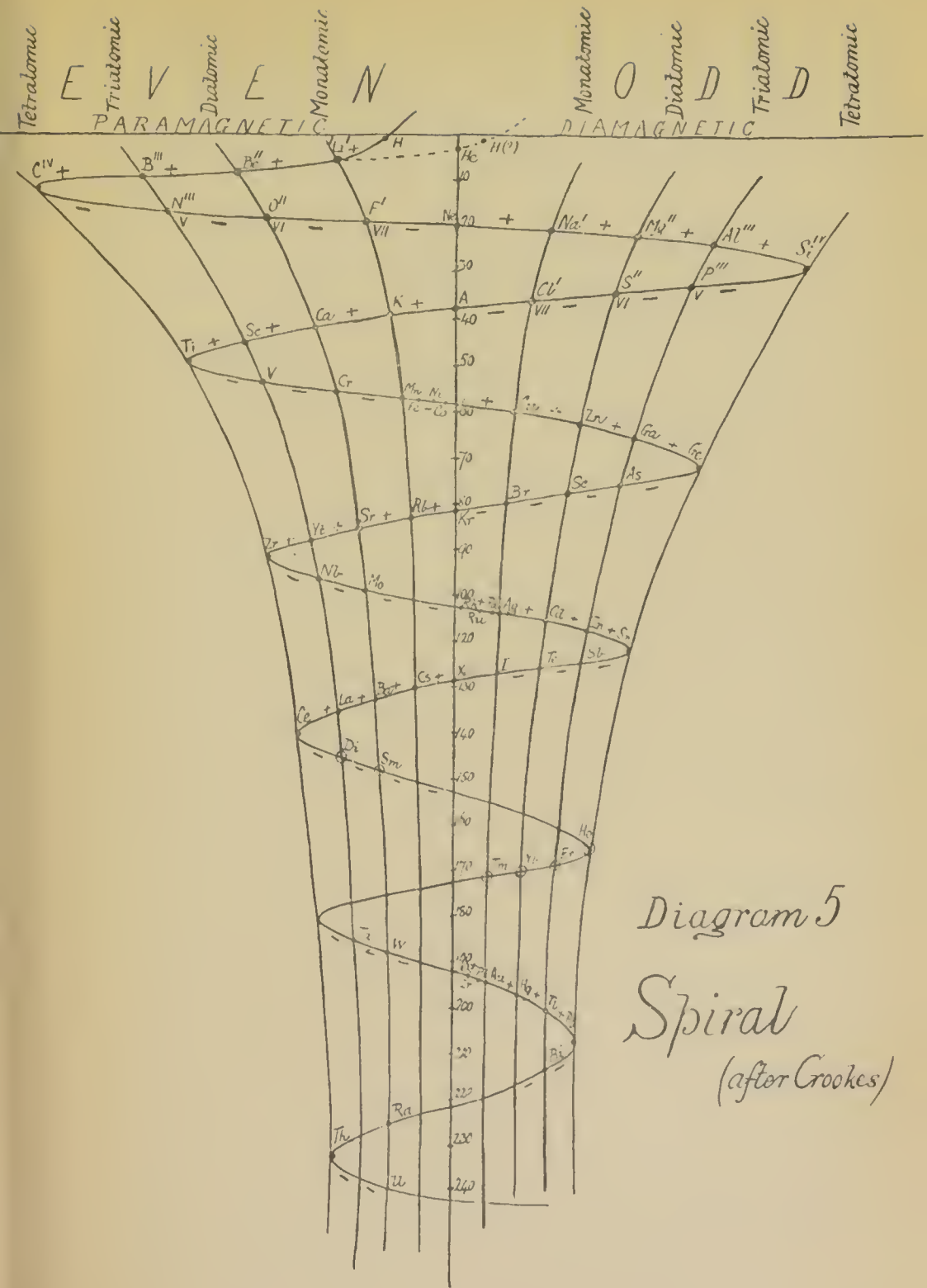


Diagram 5

Spiral

(after Crookes)

of matter have ultimately developed. Thus the atoms of hydrogen, as well as those of all the other elements, were to be looked upon as compound molecules. He also put forward the idea, that our knowledge of any particular element was perhaps after all only a knowledge of average specimens of that element; and that even in such a fundamental property as atomic weight, it might be possible for variations between certain limits to occur for one and the same element.

Thus he says the majority of calcium atoms may have an atomic weight of 40, and so we are justified in looking upon this as the true atomic weight. On the other hand, some may have an atomic weight 39·9, to be counterbalanced by others of atomic weight 40·1; and so on. If this were true, then of course the properties which we perceive in any element are really the mean of those due to many slightly different atoms, differing, it is true, by ever such a minute quantity, but still not absolutely identical.

The diagram given, which is due to Sir Wm. Crookes, is really a slightly modified form of that given by Professor Emerson Reynolds in 1886,[1] by means of which the swing of a knotted string was used to illustrate the periodicity of the properties of the elements. If we accept the idea that our elements are only "average elements," then there will be a gradation between one element and the next of greater atomic weight, and the

[1] *Chemical News*, July 1886.

system of elements can be represented by a continuous curve such as that given.

The whole curve may be likened to the swings of a pendulum, which gradually decrease in magnitude as the pendulum comes to rest. The axis of the figure is graduated from 0 to 240 in order to indicate the relative atomic weights. The valency of the elements is shown by the numerals I., II.—VII., and the more usual valency which they exhibit is given in the headlines. The elements on the return branches of the curve, such as nitrogen, oxygen, fluorine, etc., have two valencies as indicated. Those to the right of the central axis are diamagnetic while those to the left are paramagnetic. With respect to their electric properties it will be noted that those on the receding branches of the curve have positive properties, while those on the approaching branches are electro-negative. To such general rules as these one is not surprised to find exceptions. The most noticeable are that sodium, magnesium, aluminium, silicon, platinum, and palladium, which according to this arrangement are included with the diamagnetic elements, all show distinct paramagnetic properties; also iron, cobalt, and nickel ought to be with the electro-positive elements. Of course the elements of the argon group were not included in the original diagram, but it will be noted that they fit fairly readily into their positions on the line of zero valency. If the line which starts the curve is allowed to begin slightly to the right of the axis, then helium would have a place on the curve.

but hydrogen must then be slightly displaced. Argon, as in the periodic table, requires a slightly smaller atomic weight in order that it may fit into position in front of potassium. Radium falls into position as an analogue of barium if the atomic weight 226 is accepted.

The members of Mendeléeff's group VIII. are placed between two nodal points. These elements are looked upon by Crookes as interperiodic, because they are excluded from the short periods by reason of their atomic weights, and also because their chemical properties are such, that they form a sort of transition stage between the members of neighbouring groups. The even and odd series are also indicated, and it should be noted that analogous elements are on the same vertical line, but only on similar branches of the curve, that is either receding or approaching. For example, calcium, strontium, and barium all lie on line two to the left, and on receding branches of the curve.

Crookes called attention to the fact, that those elements which have been discovered by spectroscopic means, viz., gallium, indium, thallium, rubidium, and cæsium, fit into position on the curve; while some few elements such as didymium,[1] erbium, thulium, and ytterbium, are out of place. These latter elements it will be remembered have not been absolutely fixed in Mendeléeff's table. It may be well to point out that this system requires sulphur to be bivalent, and manganese to be monovalent, although manganese can be referred to the

[1] Not now considered as an element.

univalent elements only by analogy in such compounds as $KMnO_4$, and $KClO_4$. Similarly uranium is considered as bivalent, without any apparent good reason for so doing.

In using this arrangement to explain the genesis of the elements from the original protyle, it was assumed that as a matter of course the first-born of the elements would be the simplest, and would be the nearest approach of any of the elements to the original protyle in its properties. This post of honour then falls to hydrogen, which in such a scheme must be regarded as the simplest element on account of its small atomic weight. This element hydrogen, would be for some time the only one in existence, then as cooling down proceeded, the protyle gradually became changed into other and different elements. The longer the cooling down process took in order to bring about the change, the more clearly defined would be the element so produced, while any rapid cooling which took place, would result in the birth of a series of closely allied elements, the properties of which would gradually alter from one member to the next in an all but imperceptible manner; such are the elements occupying group VIII. The curve itself may be taken to illustrate the changes in the action of two forms of energy. One kind may be supposed to be acting in a vertical direction, and the other in a vibratory manner. The vertical line will represent the changes of temperature consequent upon a gradual sinking through the unknown number of degrees which repre-

sents the difference between the temperature of the dissociation point of hydrogen, and that of uranium. The other form of energy which is connected with the line vibrating to and fro to points equidistant from the central axis, which axis may be looked upon as a neutral line, confers varying degrees of valency upon the elements, as the distance from the neutral line increases. Also, when receding from the neutral line it impresses an electro-positive nature upon the elements and when approaching it renders them electro-negative. Hence Crookes says, "We are led to suspect that this oscillatory power must be closely connected with the imponderable matter, essence, or source of energy we call electricity." He further called attention to the fact that carbon, the most common element in the organic kingdom, stands at the beginning of this oscillatory curve; while at the opposite end of the same swing stands silicon, the element which is the most common of all in the inorganic world. Again, following after carbon we have nitrogen, oxygen, and fluorine, all of which elements enter into organic compounds, and which are of a gaseous nature when in a free state; while coming back towards the central line from silicon are the elements aluminium, magnesium, and sodium, all of which are prominent in the inorganic world.

So that he says: "In the first complete swing we have formed the elements of water, air, of ammonia, of carbondioxide, of plant and animal life. We have phosphorus for the brain, salt for the sea, clay and sand

for solid earth; two alkalies, an alkaline earth, along with their carbonates, borates, nitrates, fluorides, chlorides, sulphates, phosphates, and silicates, sufficient for animal and vegetable life and for a world not very different from our own."

The curve is unfinished at its upper end, and this is taken to indicate that other forms of matter with which we are not familiar may have an existence, and a place in this scheme above the zero line. The question is asked, "Is electricity one of these negative elements, and the luminiferous ether another?" From spectroscopic analysis of the light received from nebulæ it appears that the number of elements in existence in those bodies is very limited. Hydrogen and helium are usually found to be present, and one or two other substances as yet undiscovered terrestrially also contribute lines to the spectrum.

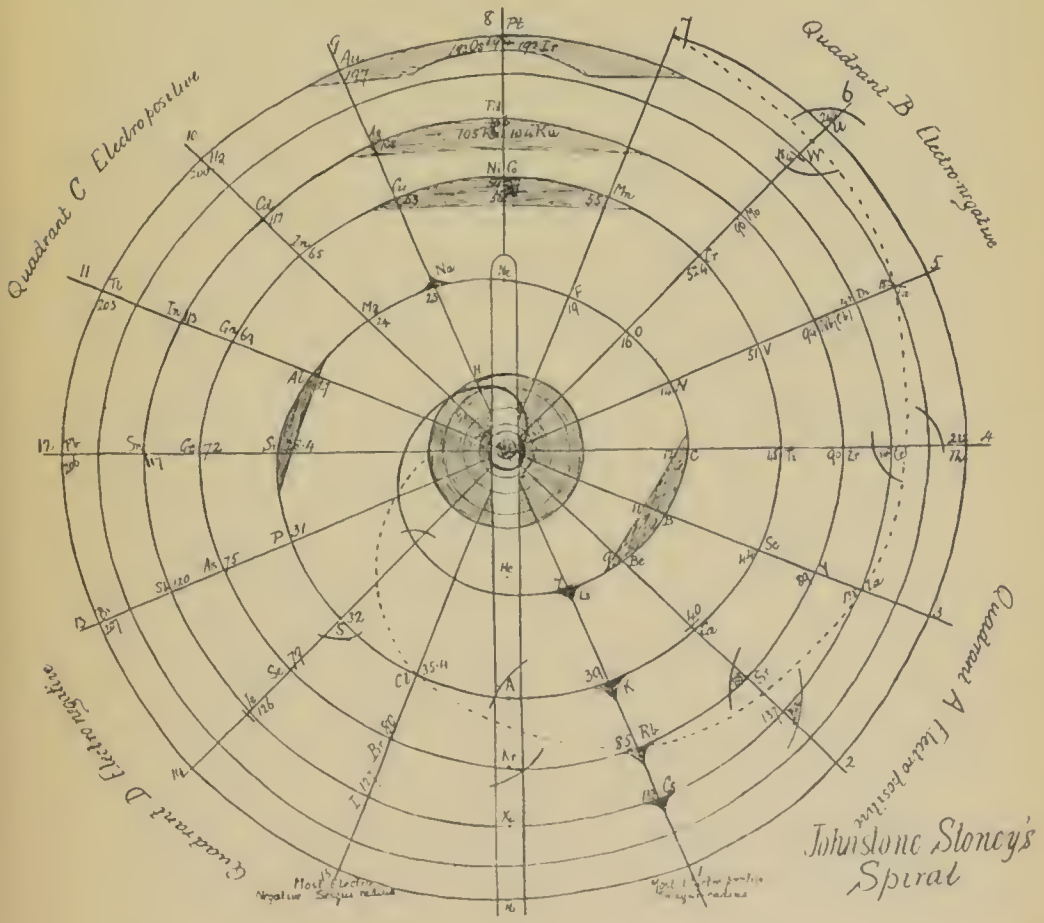
In some of the nebulæ only hydrogen and the two unknown substances appear to be present. Hence it is only natural that attempts should be made to account for our present system of the elements by some such arrangement as that just described.

Johnstone Stoney [1] claims that a spiral when referred to polar co-ordinates makes the chemical grouping of the elements more conspicuous. The following diagram, which is due to Stoney, illustrates such an arrangement.

The spiral he proved to be a logarithmic one, although except for the innermost turns an elliptic

[1] *Phil. Mag.* [6], 4, pp. 411 *et seq.*; *Proc. Roy. Soc.*, 1888, p. 115.

equation would represent the curve just as well. There are sixteen lines radiating from the starting-point and these lines are equally inclined to one another. The points at which these lines are crossed by the spiral



indicate the positions occupied by the elements. The atomic weights of the elements are represented by volumes on this system. The atomic weight of hydrogen is represented by the volume of the globe in the centre, and those of the other elements by spheres, the radii

of which are equivalent to the distances of the points representing the elements, from the starting-point of the curve. The elements possess atomic weights which when represented in this way are such, that they with very few exceptions are placed where the curve cuts the radiating lines. The elements hydrogen, lithium, calcium, iron, tellurium and tungsten are the only ones in which the deviation can be shown on a small diagram. The dotted spiral, and the small curved lines shown on the diagram, also refer to deviations. It will be seen that according to the diagram these deviations from the curve depend upon a period of 18 places, while chemical and physical properties depend upon a complete revolution or period of 16 places. It was found by Johnstone Stoney that the deviations follow one law in the case of elements of even atomicity, another slightly different in the case of those of odd atomicity, although both laws depend upon a period of 18 places.

He further pointed out, "it is the existence in nature of these deviations, that renders possible an apparent reversal of Mendeléeff's order of succession such as most certainly prevails between tellurium and iodine, where the element to which we must assign the greater atomic weight comes first in the ascending series."

He uses the term sesqui-radius to indicate the whole of one radius vector together with the inner part of the continuation of that radius; this is shown in the diagram for sesqui-radius 16, or again for the halogens fluorine chlorine, bromine, and iodine on sesqui-radius 15. The

elements contained in the same quadrants are all either electro-positive or electro-negative, the quadrants being alternately electro-positive and electro-negative, and the transition from one quadrant to the next is gradual except between quadrants A and D. The groups into which the elements are divided by Johnstone Stoney's spiral according to their electric properties are identical with those obtained by Crooke's arrangement. The elements of Mendeléeff's eighth group and the argon family also occupy interperiodic positions on this spiral.

The shaded prominences are used to denote those elements of relatively great atomic volume in the solid state, while the shaded sectors indicate those which possess relatively small atomic volumes. The elements of the argon group find suitable positions on sesqui-radius 16 between the most electro-positive and most electro-negative groups of elements. Johnstone Stoney showed in his original memoir that he had sound reasons for the introduction of sesqui-radius 16, and this is all the more remarkable since none of the argon group had been discovered when that paper was written. In concluding his remarks upon the curve he said, " If as seems probable a logarithmic law is the law of nature there appears to be three elements lighter than hydrogen. Yet these depend upon the probability that the log-curve is to be employed for elements lighter than lithium rather than the elliptic curve, or any other which can like these thread its way amid all observed atomic weights from lithium to uranium."

When helium was discovered and its atomic weight found to be 4, it was found that its position could not be represented on the curve, but it had to be placed as shown on the diagram. This seems to render it less probable that the prophecy of the preceding paragraph should ever be fulfilled. On comparing the arrangements of the elements into families, according to these two spirals, with those of the periodic table of Mendeléeff, it will at once be seen that the groupings are practically identical for all three, thus affording still further evidence that the periodic table gives a natural classification of the chemical elements.

CHAPTER VII

OTHER APPLICATIONS OF THE PERIODIC LAW

In this chapter several interesting instances in which the Periodic Law can be applied are dealt with; these, as a rule, have no direct connection one with another, and for that reason each division of the chapter can be considered as complete in itself.

The Spectra of the Elements.—When the temperature of an element is raised sufficiently to cause it to emit light, the colour of the light so emitted depends upon the element under examination. If the light be examined by means of a spectroscope it will be seen when the temperature is sufficiently high to vaporize the material, that the spectra emitted by each element consists of a definite number of bright lines, and these lines are invariable for the same element under the same conditions of temperature and pressure. The elements of the alkalies yield line spectra when placed in the flame of the bunsen burner, but those of the alkaline earths yield spectra which are composed partly of lines, and partly of bands when they are subjected to the same treatment.

When the heat is increased to that obtainable with the aid of the oxyhydrogen flame, the following elements

can be classified into the groups as arranged below, by means of the lines which are visible in their spectra.

I.	II.	III.	IV.	V.
Lithium	..	..	..	..
Sodium	Copper	Magnesium	Calcium	Aluminium
Potassium	Silver	Zinc	Strontium	Gallium
Rubidium	Gold	Cadmium	Barium	Indium
Cæsium	..	Mercury	..	Thallium

The elements in these groups have been so classified since they gave spectra which on the whole are very much alike in the number of bright lines visible, and the groups into which these lines may be divided, except for the fact that they have been bodily shifted a small distance either towards the violet or red end of the spectrum. Moreover, as can be seen by the list given, the elements of which this is true are those which belong to the same sub-group of elements.

On the other hand it is worthy of note, that if the elements are considered in the order in which they occur in any series, that is with increasing valency but little increase in atomic weight, the result so far as their spectra are concerned, may be that the whole of a series of lines is displaced much more than would be accounted for by the change of atomic weight.

These lines which are made use of in grouping together like elements, are considered as "corresponding" or "homologous" lines for any particular group of ele-

ments, and they must exhibit the same optical characteristics to be so classed. Thus the calcium line 4226(7), the strontium line 4607, and the barium line 5536, are corresponding lines.

When a salt of one of these elements is used to produce a spectrum, the line just named is the principal line which is observed in each case if the source of heat is the flame of a bunsen burner. When the spectrum of any one of these elements is obtained by means of the electric arc, the lines named behave in an exactly similar manner, being broadened and easily reversed; lastly, when the source of light is placed under the influence of a magnetic field they are each split into three components of a rather broad type, and the spacing as measured by the scale of oscillation frequencies is the same for all three spectra.

Again, the red line of lithium, and the D lines of sodium are the strongest in the spectra of those elements, and are likewise corresponding lines.

Now Ditte[1] found with reference to the elements chlorine (group VII. series 3), bromine (group VII. series 5), and iodine (group VII. series 7) that with an increase of the atomic weight, that is in passing from chlorine to bromine to iodine the spectra observed expand gradually towards the ultra-violet end. Each spectrum has two maxima of light which approach each other as the atomic weight of the element increases. The brightest lines of the spectra seem to become broader,

[1] *Comptes Rendus*, 1871, lxxiii., pp. 738-742, 622.

and the positions of the maxima shift towards the violet end as we pass from chlorine to bromine and iodine.

The spectrum of fluorine differs in many respects from those of the other three halogens, for, although there are two well-defined maxima of brightness, yet it does not present the brilliant region peculiar to the spectra of the chlorine group, and besides, the maxima are much more widely separated.

In the sulphur group, that is the elements sulphur, selenium, and tellurium, the spectrum in each case shows two maxima of brightness, and they shift slightly towards the violet end, and each spectrum increases in range towards the violet end with an increase of the atomic weight of the element used.

The spectra of the elements of the phosphorus group, viz., phosphorus, arsenic, antimony, and bismuth, behave in a precisely similar manner except that each of these exhibit three points of maximum brightness instead of two.

According to Trooste and Hautefeuille [1] the spectra of carbon, silicon, titanium and zirconium appear to be in accordance with the rules just given for the other sub-groups. Aluminium, gallium, indium, and thallium, are characterized by the fact that the lines shift gradually towards the red end as the atomic weight of the element used increases; thus aluminium has very characteristic bands in the ultra-violet besides lines in the blue and red, gallium has two violet lines, indium gives an intense

[1] *Comptes Rendus*, lxxiii. pp. 620-622.

indigo blue line and a less intense violet line, while thallium gives an intense green line.

The calcium group, calcium, strontium, and barium; the potassium group, lithium, sodium, potassium, lead, and cæsium; and the copper group, copper, silver, and gold, all follow the same rule although sodium and lithium appear to be exceptions.

The magnesium group with the exception of zinc follow the first rule.

Lockyer[1] found that for the halogen compounds of lead (PbF_2, $PbCl_2$, $PbBr_2$ and PbI_2), the length and number of the lines observed which are due to the metal, diminish as the atomic weight of the halogen increases. The same also holds true for the compounds formed by the metals of the alkalies and the alkaline earths, with the halogens.

Mitscherlich[2] observed that for the barium compounds the distances between the most prominent lines, at least for the chlorides, bromides, and iodides are directly proportional to the molecular weights of these compounds, while for the elements strontium and calcium these distances are inversely proportional to the molecular weights of the compounds.

Among the connections which have been noted between the atomic weights of the elements belonging to the same group or sub-group, and the characteristic lines

[1] *Proc. Roy. Soc.*, 1873, p. 285.

[2] *Phil. Mag.* [4], xxviii. pp. 169-189 (a translation from *Pogg. Ann.*); *Pogg. Ann.* cxxi. pp. 459 *et seq.*

observed in their spectra, may also be mentioned one which is perhaps most easily noticed in the elements of the zinc group. In this group an increase in the atomic weight of the element produces a shift of the lines of the spectrum towards the red end, and the amount of shift is moreover found to depend upon the squares of the atomic weights of the elements. This is by no means a general law, but it is one which applies with a fair degree of accuracy in some cases.

Thus in the sub-group zinc, cadmium, and mercury, taking the atomic weight of cadmium as 112·4, that of zinc by calculation is found to be 65·11, which is very near its accepted atomic weight, 65·4; and for the elements indium and gallium, if the atomic weight of indium is taken as 115 then that of gallium becomes by calculation 70·67 instead of 70·0 as according to the best determinations. As still further applications of the way in which the atomic weight of an element can be calculated when the differences between the oscillation frequencies of corresponding lines in that element, and one belonging to the same sub-group, and the atomic weight of the latter element, are known; instances may be taken from the calcium and potassium groups. Thus if the atomic weight of barium is 137·4, and that of calcium 40·1, then that of strontium calculated by this means becomes 87·8, instead of 87·6 as accepted, while that of rubidium calculated from those of cæsium and potassium is also found to be extremely close to the best experimental results.

This point will be still further considered with reference to the position of radium in the periodic table.

Rydberg and others have attempted to establish formulæ by means of which the relation between elements of the same sub-groups could be represented. Thus denoting by 'v' the difference in oscillation in the case of (a) members of doublets, and (b) the two more widely separated lines in triplets, Rydberg found that the value of 'v' increases in special sub-groups with an increase in the atomic weight, and that 'v' could be represented as a complicated function of the atomic weight. He made these observations entirely on the subordinate series of lines, and he found that the values of $\frac{10^3\, v}{(\text{Atomic Weight})^2}$ were periodic functions of the atomic weight. He also gave the formula $n = n_\infty - \frac{N_0}{(m+\mu)^2}$ to include all the series of harmonic lines in the spectra. In this formula $n = 10^8 \lambda^{-1}$, where λ represents the wave-length of the light, n_∞ and μ are constants for each particular series, and N_0 is a constant common to all the series, while $m = 1$, 2, 3, etc. This formula gives better results for elements having low atomic weights, and the differences between the calculated and observed values increase as the atomic weight of the element under observation increases.

Kayser and Runge have also given a formula for calculating $10^8 \lambda^{-1}$. It is $10^8 \lambda^{-1} = A - Bn^{-2} - Cn^{-4}$,

where $n=3, 4, 5\ldots$ and A, B, and C are constants peculiar to the series.

Colours of the Compounds.—Carnelley pointed out that the colour of the compounds of the elements is a function of the atomic weights of their constituents. Thus in any series A_mR_n, B_mR_n, C_mR_n, etc., in which R is taken to represent an element or group of elements, and A, B, C, etc., elements belonging to the same sub-group; as the atomic weight of A, B, C, etc., increases, so the colour of the compound undergoes a change, passing gradually from white or colourless through the various shades of violet, indigo, blue, green, yellow, orange, and red, to brown and black. This rule only applies so long as the observations are confined to the same sub-group of elements; on this account, oxides cannot strictly speaking be compared with sulphides, selenides, or tellurides, nor can fluorides be compared with the other halogen compounds.

The following examples will illustrate this :—

Compound.	Colour.	Compound.	Colour.
NaCl	White	Na_2Se	Red
CuCl	White	...	...
AgCl	White	Ag_2Se	Black
AuCl	Light yellowish	...	...
NaBr	White	Na_2Te	Dark coppery
CuBr	Grey	...	...
AgBr	Yellowish white	Ag_2Te	Black
AuBr	Yellowish grey	...	...

Compound.	Colour.	Compound.	Colour.
NaI	White	Na_2S	Fresh coloured
CuI	Cream	Cu_2S	Black
AgI	Light yellow	Ag_2S	Black
AuI	Golden yellow	Au_2S	Black
PI_3	Red	NaF	White
AsI_3	Light red	CuF	Red
SbI_3	Red	AgF	Brown
BiI_3	Greyish black	...	...

In the case of an increase in the weight of the acid principle the same effect is apparent, for

$CoCl_2$ is blue — $NiCl_2$ yellow
$CoBr_2$ is green — $NiBr_2$ golden
CoI_2 is black, and — NiI_2 black
$PtCl_2$ is orange — $PtBr_2$ is brown, while
PtI_2 is brownish black.

There are however many exceptions to this general rule, for the following compounds of the heavy elements, gold, tungsten, and uranium, are of a somewhat greenish colour, while according to the rule given they should be black, or at least brown, Au_2O, AuI_3; WCl_4, WI_2; and UCl_4, UCl_5. Again phosphorus bromide (PBr_5) is usually described as of a pale yellowish colour, but according to this rule it should be white. Such small differences as this may of course be due to some impurity contained in the salt. Capstick gave an explanation of this as depending on the assumptions that

in solids the molecules vibrate as a whole about certain mean positions, and that under the same conditions of temperature and pressure, the period of vibration of the molecules of solids will be smaller as the mass of the molecules diminish. If the time of the vibration is so small as to coincide with no portion of the visible spectrum, then no vibrations producing visible rays will be absorbed, and the colour of the object will be white. When from the substitution of other elements the molecular weight is increased, the time of vibration will also be increased, and it may now happen that it will coincide with the violet rays of the spectrum; if so that colour is absorbed and the compound naturally appears of the complementary colour that is greenish yellow. Gradually as the molecular weight is increased, so the period of vibration increases, and blue is first absorbed, and a yellow coloured compound results; then green is absorbed, and the colour becomes orange; then yellow too is absorbed, and the resulting colour is red; finally red also is absorbed, and the coloured compound then becomes black.

Refractivities of the Elements.—Cuthbertson and Metcalfe [1] have tried to show a relationship between the refractivities of the elements and the sub-groups into which they fall when classified according to the Periodic Law. To do this they proposed the accompanying rearrangement of the sub-groups. The sub-groups are in the vertical columns.

[1] *Phil. Tran.*, A. 207 (1906).

GROUPING OF THE ELEMENTS TO ILLUSTRATE REFRACTIVITIES (CUTHBERTSON AND METCALFE).

						H 139												
						He 144 × ½	Li	Be	B	C								
			N 297	O 270	F 192	Ne 137	Na	Mg	Al	Si								
			P 1197 299 × 4	S 1101 275 × 4	Cl 768 192 × 4	Ar 568 142 × 4	K	Ca	Se	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
Zn 2060 343 × 6	Ga	Ge	As 1550 258 × 6	Se 1565 261 × 6	Br 1125 187 × 6	Kr 850 142 × 6	Rb	Sr	Y	Zr	Nb	Mo	...	Ru	Rh	Pd	Ag	
Cd 2675 267 × 10	In	Sn	Sb	Te 2495 249 × 10	L 1920 192 × 10	Xe 1378 138 × 10	Cs	Ba	La	Ce	Di							
									Yb	...	Ta	W	...	Os	Ir	Pt	Au	
Hg 1866	Tl	Pb	Bi							Th		U						

This grouping is simply produced by a rearrangement of the sub-groups of Mendeléeff's table. The elements of the first four groups of series 3 are taken with the even series for those elements outside the central grouping, while some of the elements of series 2 are taken with the odd series in that grouping.

The figures given in the table represent the relative refractivities of those elements in which that property has been observed for the D line, while the elements are in a gaseous state. For the elements in the central enclosed group the refractivities increase more or less in the proportion 1 : 4 : 6 : 10, with an increase in the atomic weight of the elements in the sub-group under consideration. This is the relation upon which the arrangement given depends, but it is at once evident that in many of the elements there is not even a close approximation to such a relationship. Thus the values given for the elements selenium and tellurium are too low to be compared in this way with that given for sulphur. In the case of arsenic there is also a very decided discrepancy. For the single instance outside the central grouping in which the refractivities have been observed, the values obtained are still further removed from this simple ratio, and for the element mercury the value is even less than either of the values obtained for the two other elements of the same sub-group. The values of the refractive equivalents obtained by Gladstone are such as to lead to the opinion, that a maximum value is reached before the elements

of highest atomic weight, and that for those elements of higher atomic weight than that for which the refractivity is a maximum, the value decreases with an increase of the atomic weight.

The relative refractivity of the elements as given in the table will be seen to decrease from left to right, that is with increase of the atomic weight. Even although the actual values for the refractivities of the elements of the sub-groups may not exhibit any such exact relationship to one another as it was hoped to establish, the results obtained are of interest as indicating one further possible connection between the elements of the sub-groups of the periodic table.

The Hardness of the Elements.—The elements which are solids under ordinary conditions have been tested with respect to relative hardness, and tables showing the results of such experiments have been prepared. That due to Von Rydberg,[1] which is one of the most complete of its kind, is given below; in this table the hardness of the elements is given as compared with carbon (diamond) as 10.

C 10	Mn 5·0	Al 2·9	S 2·0	Pb 1·5
B 9·5	Pd 4·8	Ag 2·7	Se 2·0	In 1·2
Cr 9·0	Fe 4·5	Bi 2·5	Mg 2·0	Li 0·6
Os 7·0	Pt 4·3	Zn 2·5	Sn 1·8	P 0·5
Si 6·5	As 3·5	Au 2·5	Sr 1·8	K 0·5
Ir 6·5	Cu 3·0	Te 2·3	Ca 1·5	Na 0·4
Ru 6·5	Sb 3·0	Cd 2·0	Ga 1·5	Rb 0·3
.. ..	.. ..	.. ..	.. ..	Cs 0·2

[1] *Physikalisch-chemische Tabellen, Landolt-Börnstein*, 1905.

When a diagram is prepared in which the atomic weights of the elements are plotted as abscissæ and the relative hardness as ordinates, the periodic variation of this property with increasing atomic weight is at once apparent. The maximum point appears to occur in each period with the element which has its position just before or after the minimum point of the corresponding part of the atomic volume curve. The metals of the alkalies occupy the minima, while a secondary minimum occurs in each period, such as at phosphorus, gallium, indium, and thallium. These elements are all similarly situated on the atomic volume curve, being on the first part of the ascending portion of that section of the curve to which they respectively belong.

Of course only those elements which are solid under ordinary conditions are represented, but it is quite apparent that this property is a periodic function of the atomic weight, and that the groups into which the elements are by this means divided are similar to those obtained by means of the atomic volume curve. The hardness of molybdenum and thallium are not given in that table, but for the curve to be uniform, it requires the maximum point for each of the three long periods to be at the element which is in the sixth group of the periodic table, viz., chromium, molybdenum and tungsten respectively; and the secondary minimum for these periods to occur at the elements of the third group, viz., gallium, indium and thallium respectively. The latter is certainly true since thallium is so soft that it

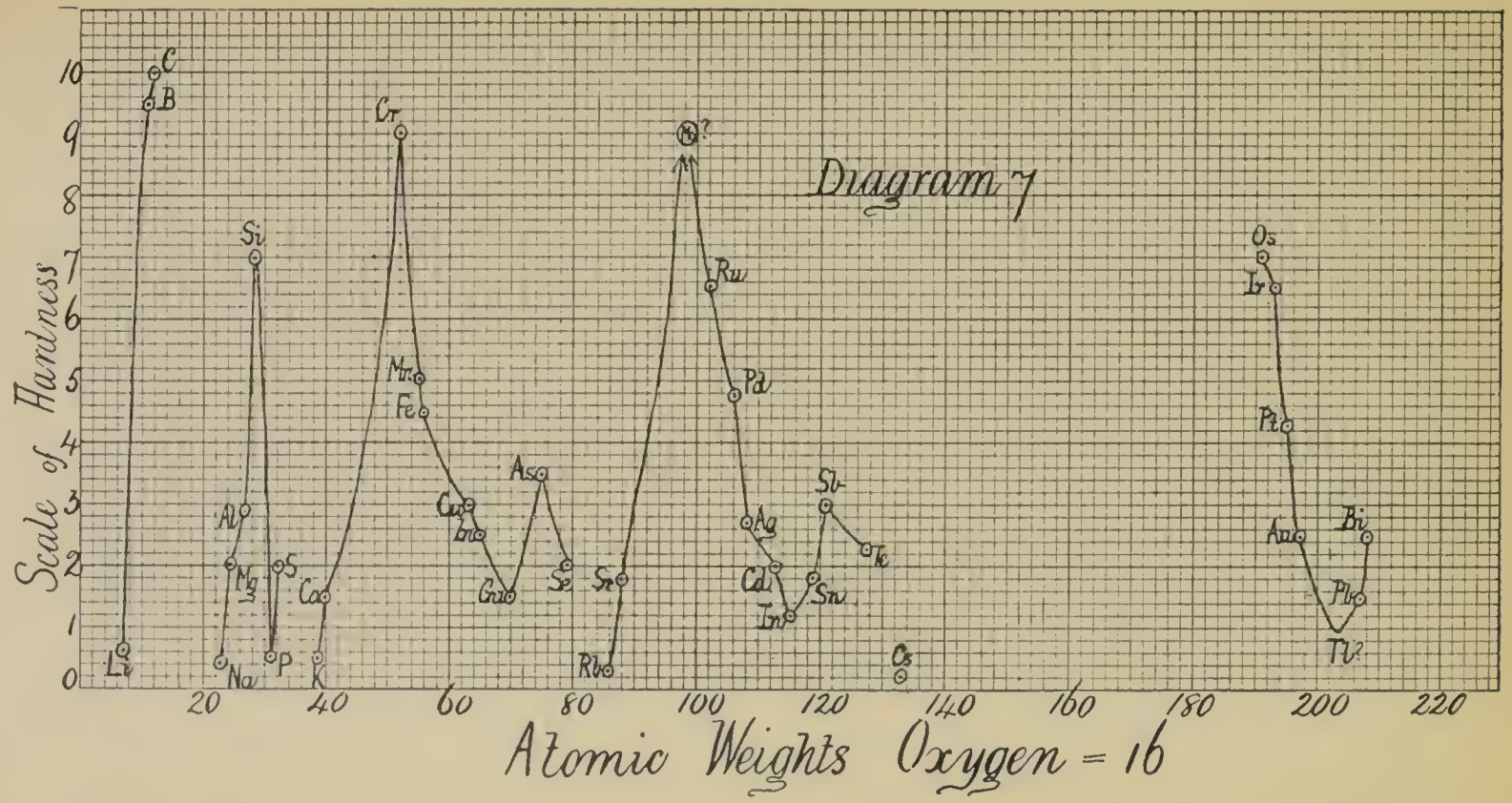


Diagram 7
Scale of Hardness
Atomic Weights Oxygen = 16
0
1
2
3
4
5
6
7
8
9
10
20
40
60
80
100
120
140
160
180
200
220
C
B
Li
Si
Al
Mg
Na
S
P
K
Ca
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
As
Se
Sr
Rb
Ru
Pd
Ag
Cd
In
Sb
Sn
Te
Cs
Os
Ir
Pt
Au
Bi
Pb
Th

can be scratched with the nail, and is softer than lead. For the elements of the first three series the maxima occur with the elements of group IV., viz., carbon and silicon respectively.

Compressibility of the Elements.—It has been shown that the atomic volumes of the elements vary periodically as their atomic weights increase, and if any real meaning is to be attached to the term 'atomic volume,' we should expect the compressibility of the elements to vary in a similar manner. A large amount of experimental work has recently been carried out by Richards [1] with the object of ascertaining the amounts of compression which the various elementary substances undergo when placed under exactly similar conditions of pressure. He arranged his experiments so that a relatively small change of pressure (one atmosphere about) took place while the elements were being subjected to a pressure amounting to between 100 and 500 atmospheres. For his unit of pressure he used the megabar, that is, the pressure of a megadyne on a square centimetre. That pressure is equivalent to 0·987 of the average atmospheric pressure.

The following diagram, in which the atomic weights are plotted as abscissæ, and the mean compressibilities multiplied by a million as ordinates, will, by its similarity in general form to the atomic volume curve, show the close relation which exists between the compressibilities of the elements and their atomic volumes. The dotted

[1] *Zeitschr. für Phys. Chem.*, 61, 1907, pp. 98 *et seq.*

lines indicate that no data were obtained for elements on that portion of the curve. Richards defines the mean compressibility as "The mean alteration of unit volume which is caused by a pressure of one megabar, for pressures of between 100 and 500 megabars."

Although the compressibility curve is the same in general form as the atomic volume curve, there are several points in which marked differences occur.

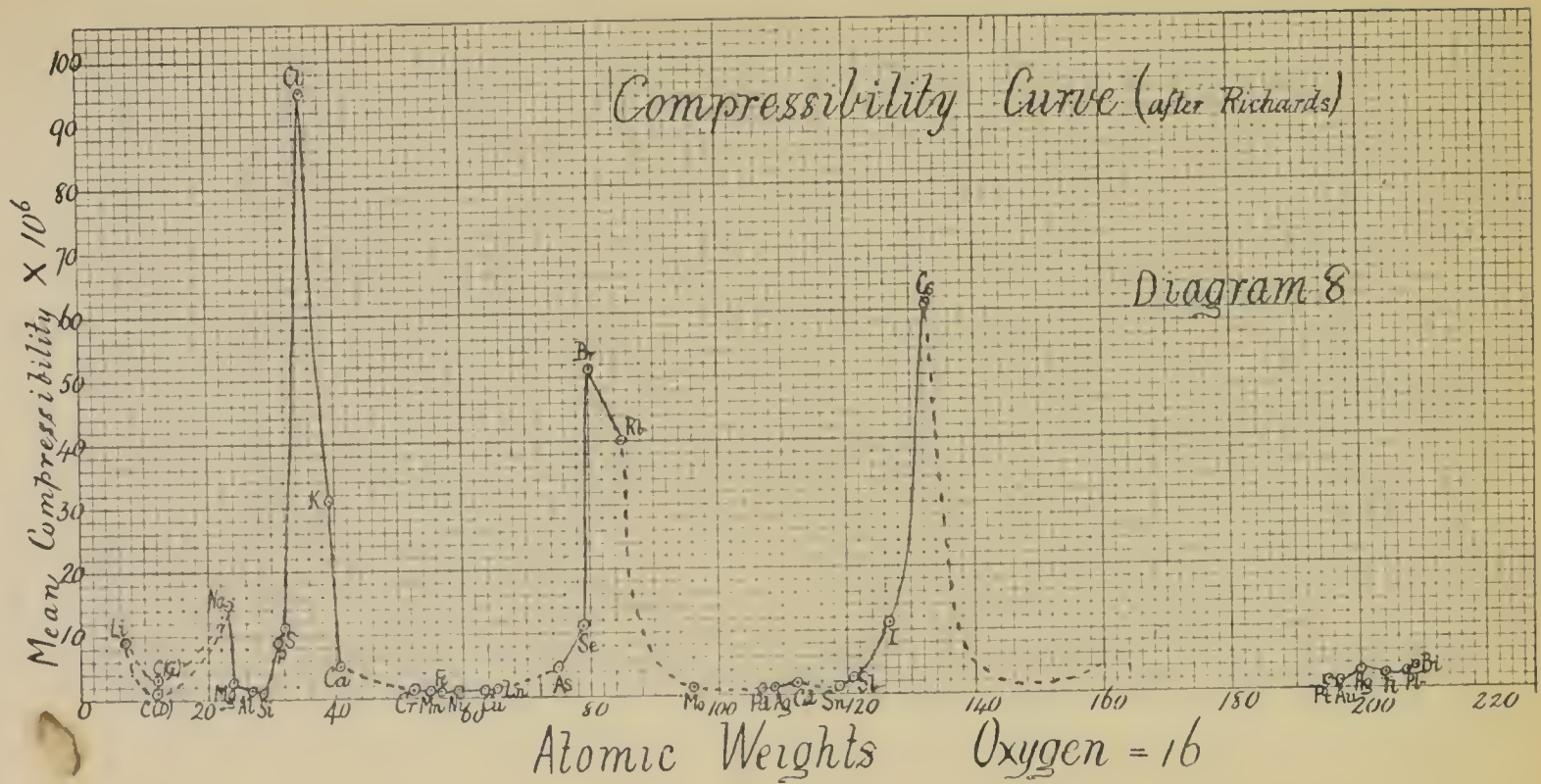
The most important of these have reference to the points of maxima. On the atomic volume curve, the alkaline elements are found in all cases to occupy such positions, but in this curve only lithium (?), sodium, and cæsium, occur at the maxima, while potassium and rubidium are on descending branches of the curve in positions similar to those occupied by calcium and strontium respectively, on Lothar Meyer's curve.

The other two maxima on the compressibility curve fall to the share of the halogens, and are occupied by chlorine and bromine.

The lower portions of both curves are occupied by the same groups of elements.

In a general sense, it may therefore be said, that those elements which have the largest atomic volumes, are the most compressible, and *vice versâ*.

The Coefficients of Linear Expansion, multiplied by 10^6, are given in the following table. The expansion has been obtained for the elements in the solid state at temperature 50° C., except for the elements, cæsium (cubical coefficient of fluid for 27° C., to 100° C., divided by


Compressibility Curve (after Richards)
Diagram 8
Mean Compressibility × 10⁶
Atomic Weights Oxygen = 16
Li
C(d)
C(g)
Mg
Al
Si
Cu
K
Ca
Cr
Mn
Fe
Ni
Co
Zn
As
Br
Se
Rb
Mo
Pd
Ag
Cd
Sn
Cs
I
Pt
Au
Hg
Tl
Pb
Bi
0
20
40
60
80
100
120
140
160
180
200
220
10
30
50
70
90

three), chlorine (cubical coefficient of fluid for −102° C., to −33·6° C.), mercury (cubical coefficient of fluid for 0° to 100°), iron (linear expansion of solid 0° C. to 100° C.), iodine (linear expansion of solid −190° to 17° C.), potassium (linear expansion for 0° C. to 50° C.), sodium (linear expansion 0° C. to 50° C.), phosphorus (linear expansion 16° C. to 42° C.) and bromine (cubical coefficient of liquid).

The elements exhibiting the greatest amount of expansion are sodium, potassium, cæsium, and chlorine, bromine, iodine.

There are other elements which expand more than their position on the table would appear to warrant; such are phosphorus, sulphur and indium. With these exceptions it will be seen that for the even series in group I. and the odd series in groups II., III., IV. and V., there is a gradual increase in the amount which represents the coefficient of expansion, with an increase of the atomic weight. For the odd series of groups VI. and VII. and the elements in the same vertical column of group VIII. there is a gradual decrease of this quantity with an increase of the atomic weight. There is a gradual increase for the elements of group VIII. which are of nearly equal atomic weights if we except rhodium, and place the atomic weight of nickel higher than that of cobalt. It would undoubtedly have been a more ideal arrangement if the coefficients of expansion of the elements had been considered for temperatures equally removed from their melting-points; such data are

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H							
2	Li	Be	B	DC 1·3 G 8	N	O	F	
3	Na 72	Mg 27·5	Al 23·3	Si 7·8	P 124	S 67·5	Cl 470	
4	K 83	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni 11·8 12·5 12·8 12·2
5	Cu 17	Zn 29	Ga	Ge	As 6	Se 37·9	Br 390	
6	Rb	Sr	Y	Zr	Nb	Mo	...	Ru Rh Pd 9·9 8·5 11·8
7	Ag 19·3	Cd 31	In 46	Sn 22·6	Sb 11·5	Te 17·3	I 83·7	
8	Cs 131	Ba	La	Ce				
9	...	...	...	...	...	...	...	...
10	...	...	Yb	...	Ta	W	...	Os Ir Pt 6·8 7 9
11	Au 14·5	Hg 61	Tl 31·3	Pb 29·5	Bi 13·6			
12	...	...	...	...	Th	U		

however not to be obtained and so the available data have been used as described.

The periodic variation of this property is sufficiently marked in the instances given.

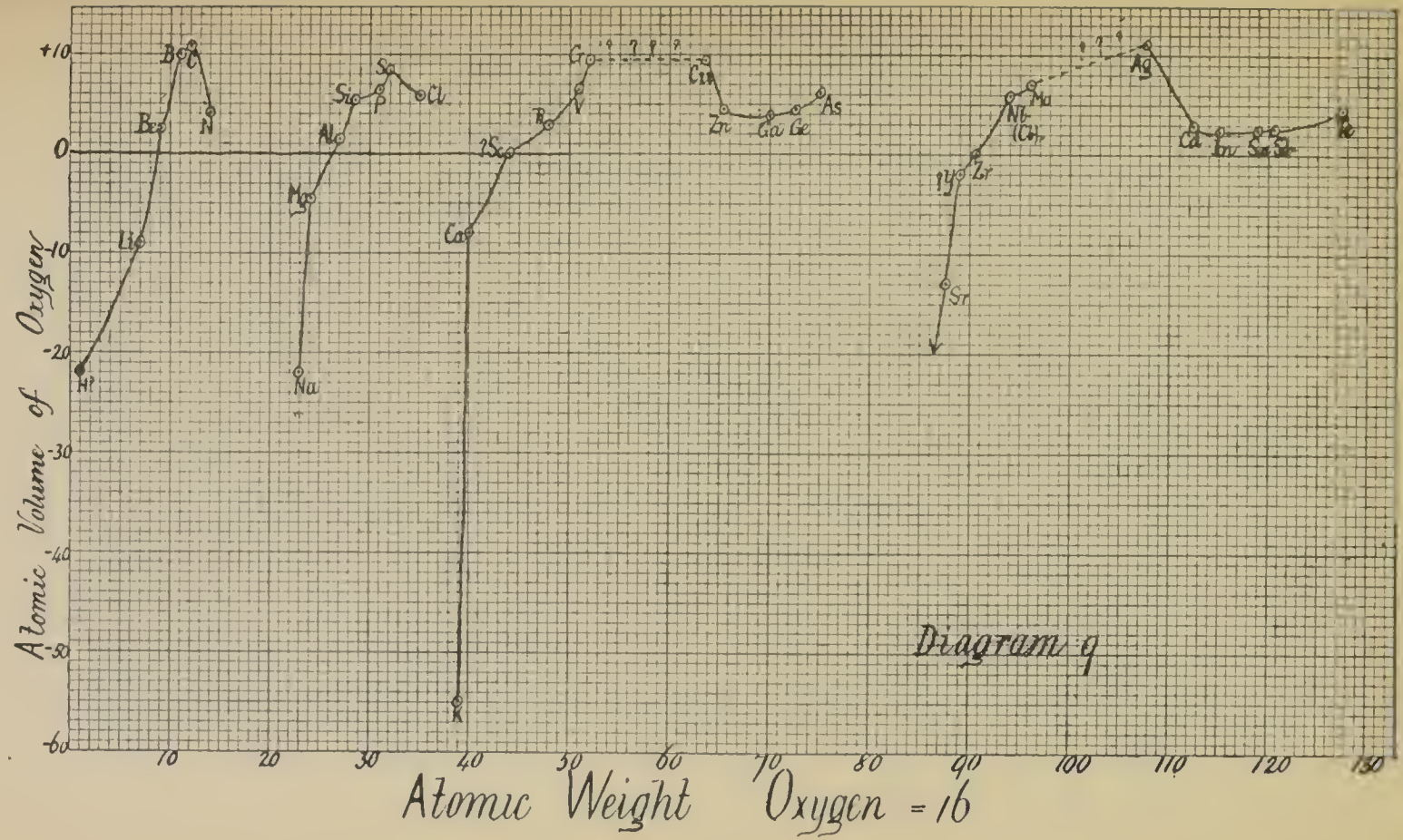
The oxides of the elements possess varying *degrees of stability* when subjected to a rise in temperature, and even this varies periodically when the elements are considered in the order of their atomic weights. The higher oxides of the elements belonging to the even series (*e.g.*, CrO_3, MoO_3, WO_3, etc.) if they are in the same group are decomposed much more readily when the atomic weight of the element is small, while the oxides of the elements belonging to the uneven series are much more stable when the atomic weight of the element is small. This is well illustrated by the oxides PbO_2, SnO_2, and SiO_2. When the elements are considered as they fall in a series instead of as belonging to a group, it is found that the higher salt-forming oxides in the even series, as for example those which lie between K_2O and Mn_2O_7 in series 4 are much more stable the lower the atomic weight of the element. For the oxides of the elements of the uneven series the stability increases from group I. to group IV. and then decreases from group IV. to group VII.

The Atomic Volume of the Oxygen in an Oxide.—If the molecular volume of an oxide is taken as equivalent to the quotient of its molecular weight by its specific gravity, and the atomic volume of the oxygen contained in the compound be considered as the difference between

that number and the volume of the element which is united with the oxygen (the difference so obtained to be considered as negative when the volume of the oxide is less than that of the element united with the oxygen), a marked periodic change will be found to take place in the volume of the combined oxygen, when the elements are arranged in the ascending order of their atomic weights.

To illustrate this take the following examples. Phosphorus pentoxide (P_2O_5) has a specific gravity of 2·4 about. Its molecular weight is $(31\times2+16\times5)=142$, so that its molecular volume according to the above definition is $\frac{142}{2\cdot4}=59$ about. Now the atomic volume of phosphorus (P) is 13·5, so that the volume of two atoms (P_2) is 27. Therefore 59 less 27, that is 32, is the volume due to the five atoms of oxygen (O_5), and that due to one atom of oxygen is 6·4. Again the atomic volume of strontium (Sr) is 35, and the volume of Sr_2 is therefore 70. The oxide (Sr_2O_2) however has a volume of only 44, so that the volume of the oxygen in combination with the strontium is 44 less 70, that is −26, and the volume of one atom of oxygen thus becomes − 13.

The accompanying diagram in which the oxygen volume for the oxides of the elements from hydrogen to tellurium is shown, indicates the periodic character of the changes which take place in those volumes. The elements in which the addition of oxygen makes but little difference in the molecular volume, that is those on or


+10
0
-10
-20
-30
-40
-50
-60
Atomic Volume of Oxygen
10
20
30
40
50
60
70
80
90
100
110
120
130
Atomic Weight Oxygen = 16
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
Diagram 9

near the zero line, such as aluminium, etc., form oxides which have only a very feeble capacity for forming salts, or in other words act only as weak bases.

The non-metals such as arsenic and phosphorus, which form acid oxides, show an increase in molecular volume when oxidised; on the other hand the oxides of the metals of the alkalies have a smaller molecular volume than the metals themselves.

Conductivity for Heat and Electricity.—These properties of the elements, which are in all probability the result of electronic movement even in the case of solids, form no exception to the periodic rule. The figures given in the following table under the heading 'heat' indicate the number of grams of water which can be raised from 0° to 1° by heat which passes, during one second, through a plane of the substance one square centimetre in area, and one centimetre in thickness, the sides of which differ in temperature by 1° C. In the column headed "electricity" are given the reciprocals of the resistance in ohms of one cubic centimetre of the substance, that of mercury at 0° C. being taken as $1{,}063 \times 10^4$. Since conductivity in both cases is a function of the temperature, the column placed next to the conductivity in each case gives the temperature at which the experiment was made. In considering the results it must be remembered that as the temperature rises the number of free electrons in the solid substance will gradually decrease because more will be able to make their escape into the surrounding medium. The groups and series

Element.	A.Wt.	Heat.	Temp.	Electricity.	Temp.	$\frac{\text{Cond. of Heat}}{\text{Cond. of Elect.}} \times 10^{-2}$	Series.	Group.
Lithium . .	7·03	...	...	$11{\cdot}9 \times 10^4$	0° C.	...	2	1
Carbon . .	12·00	...	...	$40{\cdot}8 \times 10^4$	0° C.	...	2	4
Sodium . .	23·05	...	...	$21{\cdot}10 \times 10^4$	0° C.	...	3	1
Magnesium .	24·36	0·3760	0° C. to 100° C.	$24{\cdot}47 \times 10^4$	0° C.	1·53	3	2
Aluminium .	27·1	0·3435	0° C.	22·46* / $35{\cdot}6 \times 10^4$	0° C.	1·53	3	3
Silicon . .	28·4	...	...	$30{\cdot}88 \times 10^4$	...	...	3	4
Potassium .	39·15	...	...	$15{\cdot}05 \times 10^4$	0° C.	...	4	1
Calcium . .	40·1	...	...	$13{\cdot}3 \times 10^4$	16,8° C.	...	4	2
Iron . . .	55·9	0·1665	0° C.	$10{\cdot}37 \times 10^4$	0° C.	1·6	4	8
Cobalt . .	59·0	...	...	$210{\cdot}3 \times 10^4$	20° C.	...	4	8
Nickel . .	58·7	0·1420[1]	18° C.	$19{\cdot}73 \times 10^4$ / $14{\cdot}42 \times 10^4$	0° C.	1·46	4	8
Copper . .	63·6	0·8915	18° C.	59×10^4	0° C.	1·51	5	1
Zinc . . .	65·4	0·2653	18° C.	$18{\cdot}6 \times 10^4$	0° C.	1·43	5	2
Arsenic . .	75·0	...	...	$2{\cdot}86 \times 10^4$	0° C.	...	5	5
Strotium . .	87·6	...	...	$4{\cdot}03 \times 10^4$	20° C.	...	6	2
Palladium .	106·5	0·1683	18° C.	$9{\cdot}79 \times 10^4$	0° C.	1·72	6	8
Silver . . .	107·93	1·006	18° C.	65×10^4	0° C.	1·55	7	1
Cadmium .	112·4	0·2200	0° C.	14·41* / $9{\cdot}98 \times 10^4$	0° C.	1·53	7	2
Indium . .	115	...	...	$11{\cdot}95 \times 10^4$	0° C.	...	7	3
Tin . . .	119·0	0·1528	0° C.	9·346* / 8×10^4	0° C.	1·63	7	4
Antimony .	120·2	0·0442	0° C.	$2{\cdot}71 \times 10^4$	0° C.	1·63	7	5
Tellurium .	127·6	...	...	$4{\cdot}66 \times 10^4$	19,6° C.	...	7	6
Tantalum .	181	...	...	$6{\cdot}06 \times 10^4$	...	...	10	5
Osmium . .	191·0	..	...	$10{\cdot}53 \times 10^4$	0° C.	...	10	8
Platinum .	194·8	0·1664	18° C.	9×10^4	0° C.	1·85	10	8
Gold . . .	197·2	0·7003	18° C.	$47{\cdot}4 \times 10^4$	0° C.	1·49	11	1
Mercury . .	200·0	0·0148	0° C.	$1{\cdot}06 \times 10^4$	0° C.	1·43	11	2
Thallium . .	204·1	...	...	$5{\cdot}68 \times 10^4$	0° C.	...	11	3
Lead . . .	206·9	0·0836	0° C.	$5{\cdot}04 \times 10^4$	0° C.	1·66	11	4
Bismuth . .	208·0	0·0177* / 0·0194	18° C.	$0{\cdot}924 \times 10^4$	0° C.	1·9	11	5

* Lorenz, *Wied. Ann.*, vol. xiii. p. 598. [1] Nickel, 97 per cent. [2] 99·8 per cent. cobalt. [3] Average for silicon. [4] Average for graphite.

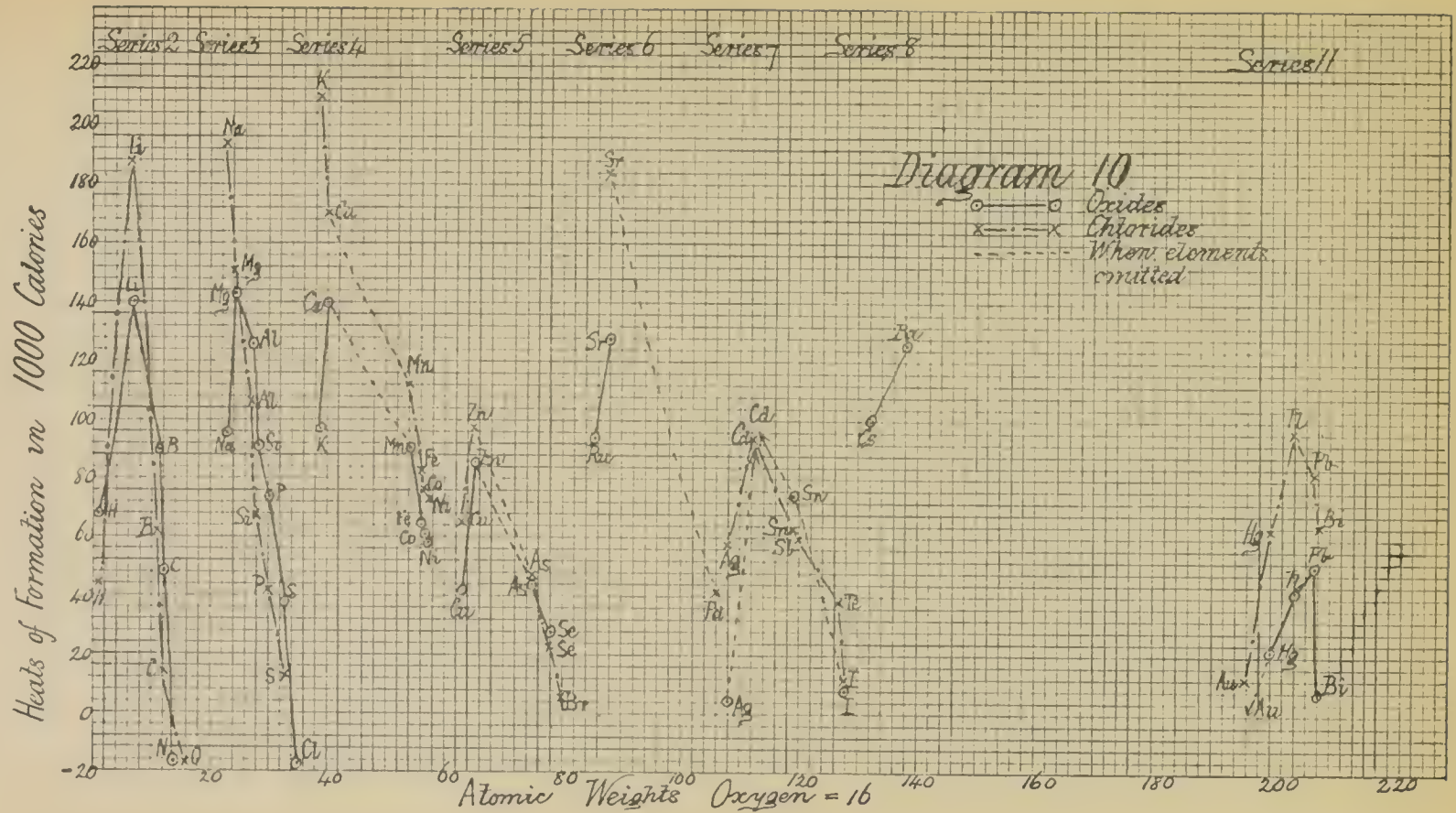
to which the elements belong are also indicated in order that the periodic variations may be recognized. For the conduction of heat there is a decrease with the increase of the atomic weight, if we except mercury, which being a liquid can scarcely be classed with the other elements, all of which are in the solid form. The elements copper, silver, and gold of group I. are all extremely good conductors. The elements of group VIII. for which the necessary data are obtainable, show a marked uniformity in their ability in this respect.

For groups II., IV., and V. there is apparently a decrease in conductivity with an increase in the atomic weights. With reference to the ability of the solid elements to conduct electricity when considered with respect to the series in which they occur, we find for those in series 3 there is an increase to group III., and then a sudden decrease; in series 7 there is a great drop between silver in group I. and cadmium in group II., then a slight increase to indium, group III., and a gradual decrease to group V. Exactly the same order of things is repeated in the elements of series II. When we examine the elements according to their groups with respect to their electrical conductivity we find the same kind of uniformity for the elements of group VIII. as is shown in their conductivity of heat; and copper, silver, and gold of group I. are again the best conductors. Among the alkalies, sodium ($21{\cdot}10 \times 10^4$), potassium ($15{\cdot}05 \times 10^4$) and cæsium ($2{\cdot}54 \times 10^4$) of group I. there is apparently a gradual decrease with increase of atomic

weight, although the data for cæsium refer to experiments on that element as a fluid at 27° C. In group II. there is a gradual decrease shown with increase of atomic weight, when the elements are regarded as of odd and even series, and the same applies for the elements of group III. odd and even series, and for the odd series of group V. In the odd series of group IV. there is first a rise of conductivity to tin, and then a fall to lead.

The very close relationship which exists between the ability of the metals to conduct heat and electricity respectively, can be seen by the column headed $\frac{\text{Conduction of heat}}{\text{Conduction of electricity}} \times 10^{-2}$. The numbers in that column all appear to approximate to the value 1·6 When it is remembered how difficult it is to obtain absolutely accurate values for the thermal conductivities of these elements the amounts by which the actual numbers in one or two instances differ from that average will be understood. That such a relationship exists was first shown by Wiedemann and Franz in 1853, and their observations were afterwards confirmed and extended by Tait, and also by Lorenz. The latter found that the above ratio, if obtained for 100° C. and also for 0° C., is just about 1·37 times as large in the former as in the latter instance. From this he concluded that $\frac{\text{Conductivity for heat}}{\text{Conductivity for electricity}}$ = a constant × absolute temperature.

The heats of formation of the oxygen and halogen


Series 2
Series 3
Series 4
Series 5
Series 6
Series 7
Series 8
Series 11
Diagram 10
Oxides
Chlorides
When elements omitted
Heats of Formation in 1000 Calories
Atomic Weights Oxygen = 16
220
200
180
160
140
120
100
80
60
40
20
0
-20
20
40
60
80
100
120
140
160
180
200
220

compounds of the elements are, as was indicated by Carnelley for the halogen compounds, a periodic function of their atomic weights. This is shown in the accompanying table in which chlorine is taken as the representative of its group.

The figures are obtained from the number of thousands of calories of heat generated in the formation of a gram molecule of the compound named, by ascertaining by proportion the amount of heat due to the union with one atom of oxygen and with two atoms of chlorine. Thus for Bi_2O_3 the heat of formation has been divided by three, and for tin chloride ($SnCl_4$) it has been divided by two, while for AgCl it has been multiplied by two.

The diagram in which the atomic weights of the elements are plotted as abscissæ, and the heats of formation as ordinates makes this relationship still more apparent.

Considering the elements by the aid of the table, according to the series in which they are placed, it will be seen that for the oxides, the heat of formation gradually decreases for series 2; for series 3, 4, 5, 6, 7 and 8 there is first a rise and then a gradual fall, the rise taking place between the first and second member of each series. In series 11 there is a rise from the second to the fourth member and then a sudden drop. The largest amount of heat is developed by the formation of the oxides of the alkalies and the alkaline earths. For the chlorides of series 2, 3 and 4 there is a gradual decrease in the amount of heat produced with an increase in the atomic weight

Heats of Formation, Oxides and Chlorides.

Elements.	Atomic Weights.	Series.	Group.	Oxides.	Heat of Formation.	Chlorides.	Heat of Formation.
Hydrogen . .	...	1	I.	H_2O	68·36	HCl	44
Lithium	...	2	I.	Li_2O	140	LiCl	187·6
Boron	...	2	III.	B_2O_3	90·9	BCl_3	62·2
Carbon	...	2	IV.	CO_2	48·48	CCl_4	14·1
Nitrogen	...	2	V.	N_2O	−17·7	...	...
Oxygen	...	2	VI.	...	...	Cl_2O	−17·9
Sodium	...	3	I.	Na_2O	Av. 96 { 100·3 / 91·0 }	NaCl	195·6
Magnesium . . .	...	3	II.	MgO	143·3	$MgCl_2$	151·0
Aluminium . . .	...	3	III.	Al_2O_3	126·7	$AlCl_3$	107·5
Silicon	...	3	IV.	SiO_2	92·25	$SiCl_4$	64
Phosphorus . . .	...	3	V.	P_2O_5	73·9	PCl_5	42
Sulphur	...	3	VI.	SO_2	38·6	S_2Cl_2	14·3
Chlorine	...	3	VII.	Cl_2O	−17·9	...	...
Potassium . . .	...	4	I.	K_2O	97·1	KCl	211·3
Calcium	...	4	II.	CaO	130·9	$CaCl_2$	169·8
Manganese . . .	...	4	VII.	MnO	90·8	$MnCl_2$	112·0
Iron	...	4	VIII.	FeO	64·6	$FeCl_2$	82·05
Cobalt	...	4	VIII.	CoO	63·8	$CoCl_2$	76·5

Nickel	...	4	VIII.	NiO	59·7	$NiCl_2$	74·5
Copper	...	5	I.	Cu_2O	40·8	CuCl	65·8
Zinc	...	5	II.	ZnO	85·4	$ZnCl_2$	97·2
Arsenic	...	5	V.	As_2O_5	43·9	$AsCl_3$	47·5
Selenium	...	5	VI.	SeO_2	28·5	Se_2Cl_2	22·15
Bromine	...	5	VII.	...	...	BrCl	1·4
Rubidium	...	6	I.	Rb_2O	94·9	...	...
Strontium	...	6	II.	SrO	128·4	$SrCl_2$	184·6
Palladium	...	6	VIII.	...	...	$PdCl_2$	40·5
Silver	...	7	I.	Ag_2O	5·9	AgCl	58·8
Cadmium	...	7	II.	...	...	$CdCl_2$	93·24
Tin	...	7	IV.	SnO	73·8	$SnCl_4$	63·6
Antimony	...	7	V.	...	...	$SbCl_3$	60·9
Tellurium	...	7	VI.	...	...	$TeCl_4$	38·7
Iodine	...	7	VII.	I_2O_5	9	ICl	11·6
Cæsium	...	8	I.	Cs_2O	99·98	...	...
Barium	...	8	II	BaO	126·4	$BaCl_2$	196·9
Tungsten	...	10	VI.	WO_3	65·5	...	...
Platinum	...	10	VIII.	...	...	$PtCl_4$	29·7
Gold	...	11	I.	...	...	AuCl	11·6
Mercury	...	11	II.	Hg_2O	22·2	HgCl	62·6
Thallium	...	11	III.	Tl_2O	42·2	TlCl	97·2
Lead	...	11	IV.	PbO	50·3	$PbCl_2$	82·8
Bismuth	...	11	V.	Bi_2O_3	6·6	$BiCl_3$	60·4

of the element, while for series 5, 7 and 11 there is first an increase and then a decrease in this quantity, the increase again occurring between the first two members except in the eleventh group in which there is an increase from the first to the third member and then a decrease. Here again then the elements of the first two groups, alkalies and alkaline earths, have the greatest heats of formation for their chlorides.

When the elements are examined with respect to the groups to which they belong, if due regard be paid to the series arrangements, there will be found to be a general decrease in the heat of formation for both oxides and chlorides except in the following cases :—

(*a*) *For the oxides* an increase from hydrogen to sodium, an increase from rubidium to cæsium, and iodine has greater heat of formation than chlorine, the latter being represented by a negative quantity.

(*b*) *For the chlorides* an increase from hydrogen to sodium, an increase for members of the even series of the first two groups, and an increase with the elements of higher atomic weight in the odd series of groups IV., V., VI. and VII.

This property apparently adds another argument in favour of nickel having a greater atomic weight than cobalt, and that of iodine being greater than that of tellurium, for the lines joining the points are more analogous if these assumptions are made.

The Position of Radium in the Periodic Table.—The atomic weight of radium has been a subject of much

dispute ever since the determinations of its value first made by Mme. Curie in 1902 and 1903.[1] She found as the mean result of her later experiments carried on during that period that the atomic weight of radium was 225, a number which she then declared to be true within about a unit. Her calculations were based upon the assumption that the element radium is bivalent, forming a chloride which could be represented by the formula $RaCl_2$; and that the atomic weights of silver and chlorine could be represented by the values 107·8 and 35·4 respectively.

She further states, that judging radium by its chemical properties, it should be placed as a superior homologue to barium in the group containing the alkaline earths. If we accept these statements as correct then radium will occupy the vacant place in the twelfth series, of the second group of Mendeléeff's table.

Mme. Curie has made some further researches into this matter, the results of which were announced in *Le Radium* for October 1907.[2] Here accepting 107·8 as the atomic weight of silver, she estimates that of radium to be 226·18 with a possible error of less than one-half a unit. These estimations were based on the quantity of silver which was required to replace the element radium in its chloride, or in other words the quantity of silver chloride which was formed by precipitating in combination with silver the chlorine of the

[1] *Annales. Chem. Phys.*, 30, pp. 137-142, Sept. 1904.

[2] See also *Comptes Rendus*, Aug. 19, 1907.

definite quantity of radium chloride used. The great difficulty in dealing with such a rare element as radium in this manner, is the extremely small quantity which it is possible to obtain for the purpose of the experiment; on this account other methods have been resorted to in which only minute quantities of the substance are required. The method based upon the spectroscopic analysis of the element is such an one. It will be remembered that elements belonging to the same subgroup give spectra which are much alike, certain lines, doublets, etc., being common to all, and again that the distances between these lines depend upon the atomic weights of the elements concerned.

Runge and Precht[1] pointed out that the strongest lines of the spectrum of radium are three pairs, and that these are analogous to those of the elements barium, strontium, etc. One pair of these lines Runge calls the primary series, and the two remaining pairs the secondary series. For the constituent lines of each of these three pairs when measured on the scale of frequency, the distance between the two lines composing each of the pairs is the same for any one of the elements included in the subgroup, provided that for the first of the secondary series, a faint line which occurs by the side of the line of greater wave length, and slightly more removed from the other line of the pair than the latter, is taken as one of the lines of the pair instead of the line against which it appears. On the other hand, the distance between the units of the

[1] *Phil. Mag.* (6), 5, 476.

pairs, varies from one element of the sub-group to another in quite a regular manner, increasing with an increase of the atomic weight. When subjected to the action of a magnetic field, the corresponding lines for each of the elements of the sub-group behave in a precisely similar manner. This is true not only for the elements magnesium, calcium, strontium and barium, but also for radium, so that on spectroscopic evidence radium should be placed in the sub-group which contains the other elements named. Rydberg, Kayser, and Runge, found that for the metals of the alkalies the distances apart of the lines forming corresponding pairs are nearly proportional to the squares of the atomic weights of the elements; also that on each group of chemically related elements the distances apart of the lines which constitute a corresponding pair vary as some power of the atomic weights of the elements.

Thus if P represent the distance apart, and q the atomic weight, this relation may be represented by the equation—

$$P=q^n. \quad \text{Therefore } \log P=n\log q,$$

or putting x for logq and y for logP we obtain the equation $y=nx$, which being represented graphically is a straight line. Hence, if the logs of the atomic weights are plotted as ordinates and the logs of the distances as abscissæ, the points so obtained, should, if the elements under consideration belong to the same sub-group, lie along a straight line.

The diagram illustrating the calculation of the atomic weight of radium has been constructed from the following data :—

Element.	Distances of Lines.	Atomic Weights.
Magnesium	91·7	24·36
Calcium	223	40·1
Strontium	801	87·6
Barium	1691	137·4
Radium	4858·5	258

The following diagrams illustrate this, and it will be seen that, for the elements of the alkali group, potassium (K) alone falls off the straight line. The position of radium which has been fixed on the other diagram by a process of extrapolation would correspond to an atomic weight of 258. The position of radium, if the value of the atomic weight as found by Mme. Curie is accepted, is likewise shown on the diagram. Should the atomic weight of radium be accepted as 258, then in order that this element may be suitably placed on the periodic table two wholly new series must be arranged, since if it is to remain in the barium sub-group it would have to be in series 14, as 258 would be out of place in series 12 of group II. In that case even 258 would be all too small a number to represent its atomic weight, assuming that the increase of the atomic weight for successive members of the same sub-group remains approximately constant. Now,

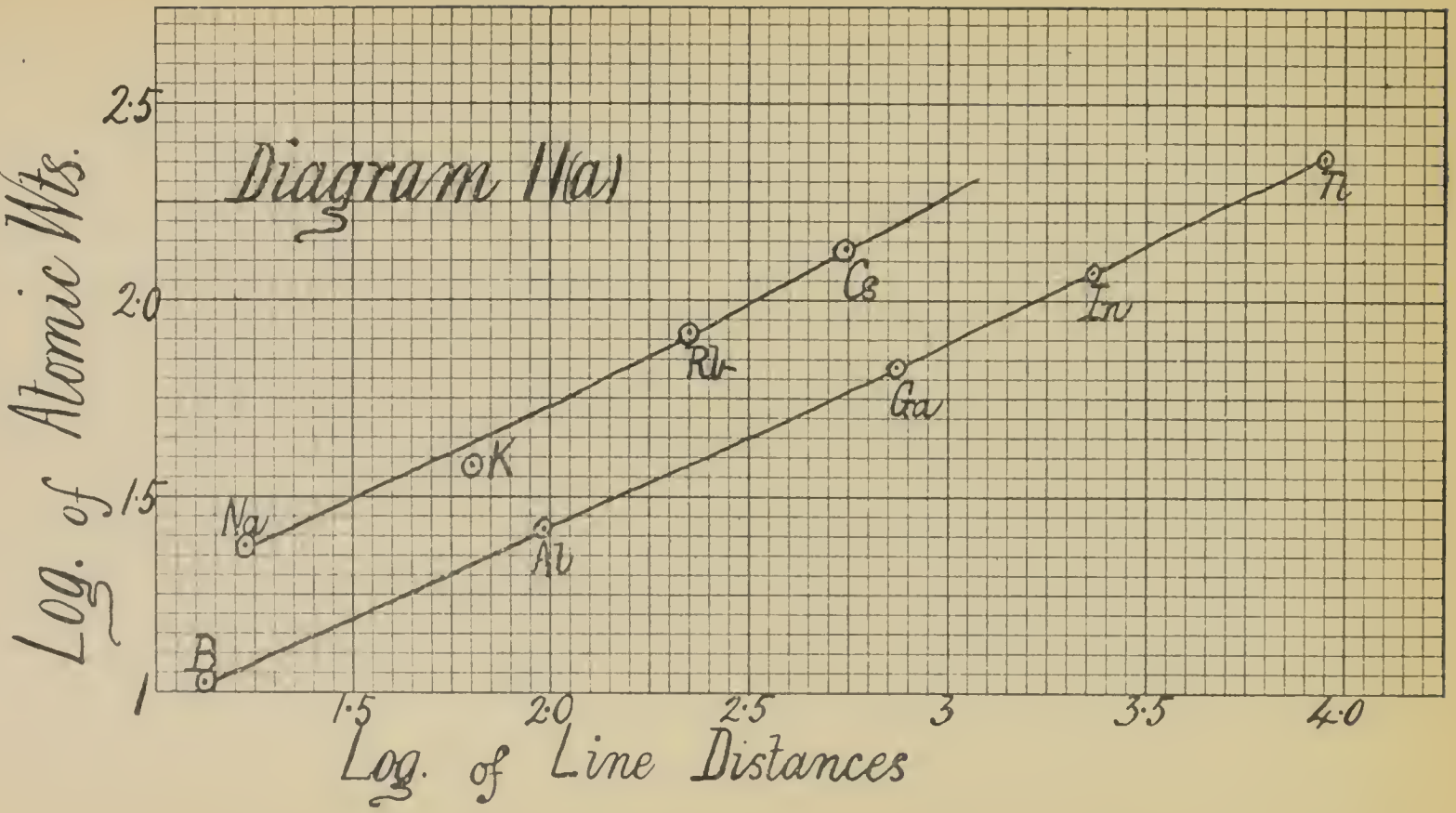


Diagram N(a)
Log. of Atomic Wts.
2·5
2·0
1·5
1
Na
K
Rb
Cs
B
Al
Ga
In
Tl
1·5
2·0
2·5
3
3·5
4·0
Log. of Line Distances

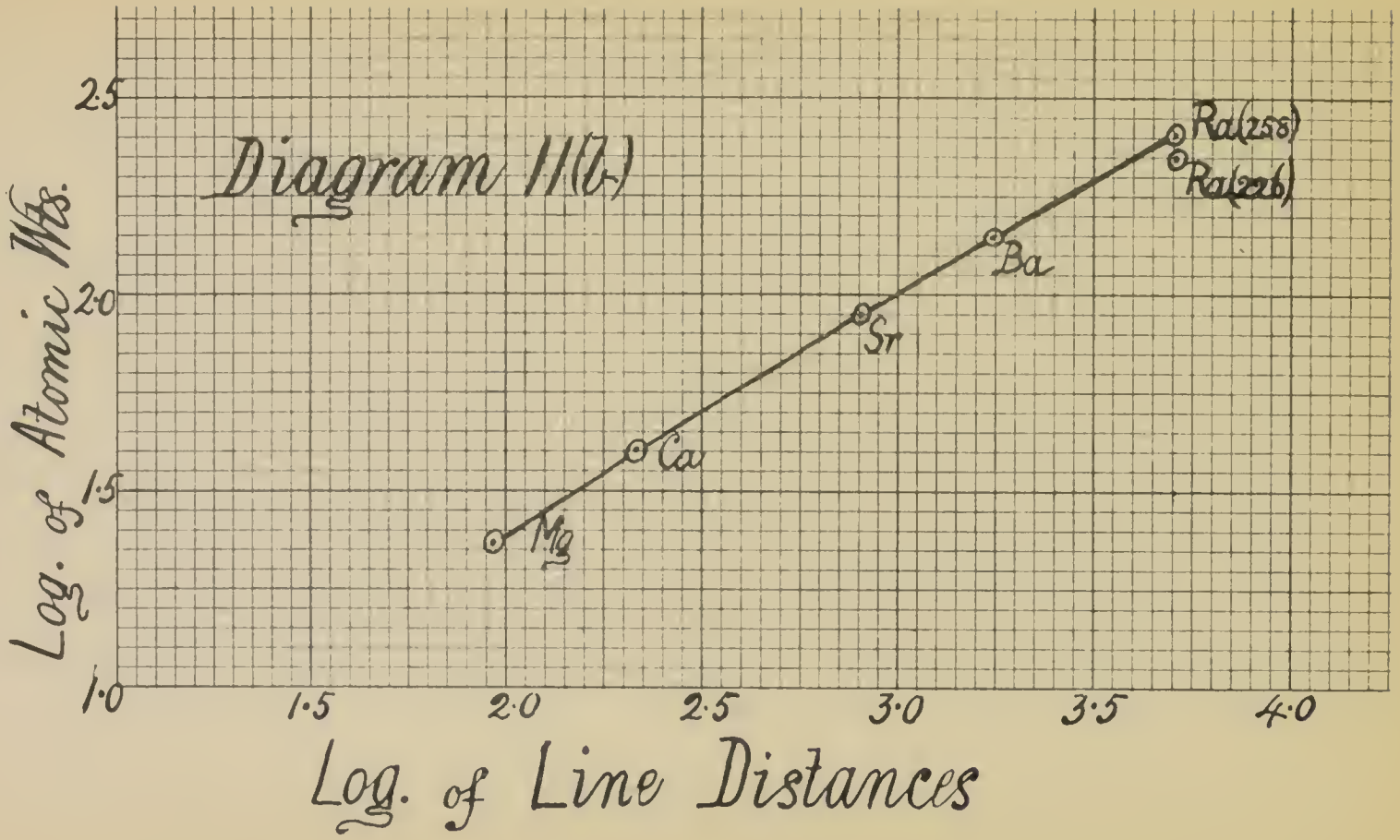


Diagram II(b)
Log. of Atomic Wts.
Log. of Line Distances
2·5
2·0
1·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
Mg
Ca
Sr
Ba
Ra(258)
Ra(226)

between the atomic weights of the sub-group to which radium belongs according to its characteristic chemical properties, we have the following relationship :—

Series.	Element.	Atomic Weight. O = 16.	Difference.
4	Calcium	40·1	
6	Strontium	87·6	47·5 } Average 48 about.
8	Barium	137·4	49·8 }
10	..	185	48
12	..	233	48
14	Radium ? ?	281	48

Thus if radium had to be placed in series 14, a greater atomic weight than even 258 might be expected. Should however the difference between series 12 and series 14 be the same as that between series 2 and series 4, viz. 31 (calcium 40·1, less beryllium 9·1), then the atomic weight of radium to occupy this position must work out at 264, a number not greatly removed from 258. Although the great proportion of experimental evidence proves to be in favour of an atomic weight of about 226, there are some arguments to be brought forward in support of a higher value for that quantity. During her investigations Mme. Curie obtained results which were successively larger as she increased the purity of the chloride with which she experimented, and although it is very highly improbable that any such error should have occurred, since spectroscopic evidence was taken in order

to prove the absence of barium, yet the presence of any such impurity would tend to greatly diminish the observed values from which the atomic weights were calculated, not sufficiently however to cause such a discrepancy as exists between 258 and the experimental result. Again, radium is one of the elements in which transformations are taking place most rapidly, and Rutherford has put forward the view, that such transformations, which are due to the discharge of electrons and α-particles, are indicative of a complex atomic structure, which is a condition necessary for elements of high atomic weight.

Marshall Watts [1] has introduced another and slightly different spectroscopic method of attacking this problem. His system consists in plotting the squares of the atomic weights as ordinates and the oscillation frequencies of the lines of the spectra as abscissæ. When this has been done he finds that the lines joining corresponding points (points on the diagram belonging to corresponding lines of two elements of the same sub-group) in homologous spectra, intersect on the zero line of atomic weight. Again if the corresponding points of three such spectra are compared, they will be found to lie along a straight line. Making use of these two properties of the line spectra of analogous elements, he has calculated the atomic weights of some elements when those of two others in the same sub-group are supposed to be known. Thus taking the atomic weight of calcium as 40·1, and that of

[1] *Phil. Mag.* (6), vi., p. 74, and (6), viii., p. 279.

strontium as 87·6, the atomic weight of barium can be calculated if we assume that the homologous lines in the three spectra have some physical connection, and that when plotted as stated above, the corresponding points for the three spectra lie on a straight line. In this way 137·46 is obtained as the atomic weight of barium.

It seems that some such relationships also exist between the spectra of mercury, barium, calcium, and radium. When the atomic weight of radium is calculated by the aid of lines meeting on the zero of atomic weight, if compared with barium it becomes 225·05, while it becomes 224.89 when compared with mercury.

Results still more close to the best experimental determinations are found, when it is assumed that the corresponding points of the spectra of analogous elements when plotted as above lie on a straight line.

Calculating from barium as 137·4 and calcium as 40·1, the atomic weight of radium by this method becomes 226.32, and from mercury as 200 and barium as 137·4 the result obtained is 226·42.

Runge and Precht's method of calculation tends to make the atomic weights obtained too high, thus for example, that of mercury when calculated by this method from the difference between the first and second lines of the triplets of the spectra of zinc, cadmium and mercury becomes 224·48. The great difficulty in all such experimental determinations seems to lie with the choice of such lines as shall be truly homologous, since if this is not done, any wished-for result may be

obtained by a careful selection of lines to suit the object in view.

Professor Thorpe made the atomic weight of radium the subject of his Bakerian Lecture in 1907. After the most carefully carried out experimental work he found that atomic weight to be 226·7. The method adopted by him was to determine the amount of silver chloride yielded when a reaction takes place with a weighed quantity of anhydrous radium chloride. A method was adopted by means of which the whole of the operations of drying and weighing the radium chloride; precipitating, washing, drying, and weighing the silver chloride, were able to be performed in the same vessel. In his calculations he assumed the atomic weight of silver to be 107·93 and that of chlorine 35·45.

Thus it seems that 226+(a fraction of a unit) may be looked upon as the true atomic weight of radium; in which case it falls into position in series 12 of group II. as the homologue of barium, the bromide of which is isomorphous with radium bromide.

The Radio-active Emanations and the Periodic Table.—Radium, as previously pointed out, is an element which is slowly undergoing a transformation into other substances of lower atomic weights. The positively charged α particles which are given off by it have a mass which has been proved by Rutherford to be about equivalent to the mass of a helium atom.[1] Besides these particles

[1] Rutherford and Geiger, *Proc. Roy. Soc.*, A 81, Aug. 1908; see also *Phil. Mag.* 17, pp. 281-286, Feb. 1909.

radium also gives off a kind of gas which must be looked upon as one of the products of the changes which are taking place in the radium atoms. Other elements, viz., thorium and actinium, likewise give off similar gaseous products, and these gases are now generally known by the term "emanation" with the name of the element which produces them prefixed; thus we have radium emanation, thorium emanation, etc.

These three emanations all have the power of greatly increasing the electrical conductivity of the air containing them, for they in their turn also give off α particles. Now assuming that the α particle has a mass equivalent to that of the atom of helium (4), and if it is at the same time assumed that the radium atom gives off one α particle and so changes to radium emanation, the atomic weight of the emanation must be 222, taking that of radium as 226.

As can be imagined, the amount of this emanation is so very small that ordinary methods of ascertaining the atomic weight are not applicable to this case, and it has to be found by methods based upon the diffusion of gases, and the well-known radioactive properties.

Hence it was that the earlier determinations made by using gases for the diffusion experiment of much smaller molecular weight than the emanation, all resulted in obtaining too low a value for the atomic weight. Thus Curie and Danne[1] found it to be 176, Makower 170, while Rutherford and Miss Brooks and others have

[1] *Comtes Rendus*, v. 136, pp. 13 and 14.

also obtained similar results. On the other hand Perkins,[1] who compared the rate of the diffusion of the emanation with that of mercury vapour (which is a suitable vapour for making the comparison, since mercury is monatomic, and has nearly the same atomic weight as the emanation), gives 235 as a rough determination. The radium emanation is the only one of which the atomic weight has been obtained with any degree of accuracy, for the other two emanations have such very short periods of existence, but attempts have been made to find their atomic weights relative to one another, and it has been found that the thorium emanation has a higher atomic weight than that of actinium.

Sir W. Ramsay [2] is of opinion that these emanations, which are essentially chemically inactive gases, should be classed with the argon group. Rutherford and Soddy have shown that copper oxide at red heat, red hot zinc dust, and red hot platinum black in the presence of oxygen, have no effect on the emanations of radium and thorium, at least their powers of producing electrical conductivity in the surrounding air are in no way altered by being in such surroundings.

Again Ramsay and Soddy have proved that sparking these gases in the presence of oxygen and caustic potash, and in the case of radium emanation the passage over red hot magnesium lime, in no way altered the emanation. Further, in a note to *Nature*,[3] Ramsay states that the

[1] *American Journal of Science*, June 1908.
[2] *Proc. Roy. Soc.*, A 81, Aug. 1908.
[3] *Nature*, 76, p. 269, July 18, 1907.

radium emanation when in contact with, and dissolved in water, produces a gas by its change which is mainly neon, with a trace of helium. When left in contact with copper sulphate or copper nitrate solution, the same emanation produces mainly argon, with it may be a trace of neon, but no helium. From this it appears that by its degradation this emanation produces elements of lower atomic weights belonging to the argon group. Be this as it may, there seems plenty of evidence of the chemical inertness of these gases, and on this account we are justified in considering them to belong to the same group as the other inert gases of the argon type. As to their position in this group, it will be seen that vacant spaces occur in series 9, 10, 11 and 12. Should Perkin's estimate be of the right order, then the radium emanation should occupy the vacant space in series 12 group 0, and its atomic weight ought to be about 218. If this were the case, the emanation of thorium would have to fall into series 11 with atomic weight 195 about, and this would mean that several α particles must be ejected before the thorium atom changes into thorium emanation, a state of things which very probably occurs. Again, should the molecular weight of the actinium emanation prove to be only about $\frac{1}{10}$ that of the emanation of thorium, as appears from the recent experiments of S. Russ, then the vacant space in series 9 would fall to its lot and its atomic weight should be about 150.

On the other hand, if the earlier determinations of

the atomic weight of radium emanation prove after all to be true, it should be placed in series 10 and have an atomic weight about 170, while the thorium emanation would occupy the space in series 12, and the actinium emanation would still be located in series 9 as $\frac{7}{10}$ of 218 is about 152.

We must however wait patiently for more data on this most difficult problem, before we can hope to settle it in a way which may be looked upon as in any degree final.

Rare Earths and the Periodic Table.—There are a large number of substances which are often spoken of collectively as "the rare earths," of which very little absolutely definite information is obtainable. As this is the case, their position in any table of the groups of the elements cannot be said to be in any measure determined; this of course more particularly applies to any arrangement like the periodic table in which the position occupied by any element is in some measure an index to its characteristic properties. The atomic weights of the rare earths range from 140 to 180 about, and hence so far as this factor is concerned they are eligible to occupy the many vacant spaces in series 8 and 9 of the periodic table. All these elements are however characterised by being trivalent, and so if the periodic rise and fall of the valency of the elements with the increase of their atomic weights is to be adhered to as a factor in the determination of the periodic group to which any element belongs, these elements must be

classed together in one group, just as iron, cobalt, nickel, etc., are placed together in group VIII.

Emerson Reynolds has in fact suggested that praseodymium, neodymium, and samarium should be placed with iron, etc., in group VIII. On the other hand Brauner, who has made a special study of these substances, suggests that they shall all be classed together with cerium in group IV.

He suggests a modification of Mendeléeff's table in which series 8 would appear as follows.

GROUPS.

...	0	I.	II.	III	IV.	V.	VI	VII.	VIII.		
Series.	Xe	Cs	Ba	La	Ce, etc.	Ta	W	...	Os	Ir	Pt
8	128	132·9	137·4	138·9	140-178	181	184	...	191	193	194·8

In this cerium, etc., takes the place of—

Cerium 140·25
Praseodymium 140·6
Neodymium 144·3
Samarium 150·4
Europium 152
Gadolinium 157·3
Terbium 159·2
Dysprosium 162·5
Erbium 167·4
Thulium 171
Ytterbium 172

Mendeléeff was of the opinion that the positions of these elements should be left an open question, since ytterbium, which is one of the rare earths the properties of which have been most completely investigated, fits in well with the position, series 10 of group III ; and further, Brauner's grouping would of course violate the rule as to valency.

The Argon Group.—Group 0.—In 1894 Lord Rayleigh and Sir Wm. Ramsay found that atmospheric nitrogen, which up to that time had been considered as pure nitrogen, was in reality a mixture of nitrogen with another gas of greater atomic weight. This conclusion was arrived at as the result of some experiments carried out by Rayleigh in which his object had been the comparison of the density of the nitrogen prepared from the air, with the density of that prepared from ammonia (NH_3). In every instance he found that the nitrogen prepared from the air was slightly denser than that which had been prepared chemically. This of course did not absolutely indicate the existence of some new gaseous element of greater atomic weight than nitrogen, of like properties to it, and mixed with it as a diluent to atmospheric oxygen. It was quite possible that nitrogen, by the action of atmospheric electricity, might undergo a change in which three atoms (N_3) became grouped together to form a molecule in much the same way as is known to be the case with oxygen, when it forms ozone (O_3). This would make the atomic weight appear larger than that of pure nitrogen. Rayleigh tested this

point by passing silent electric discharges through pure nitrogen, but he was unable to detect any increase in its density as the result.

Again, as the discrepancy between the densities of atmospheric nitrogen and chemically prepared nitrogen, only amounted to about one in 200, it was at first thought that it might be accounted for by a splitting up of the molecules of the latter, so that the gas tested consisted of a mixture of molecules and atoms of nitrogen, a condition which would cause the atomic weight to appear too low.

When however the air had been deprived of all its oxygen, and then the nitrogen so obtained absorbed either by magnesium of magnesium lime, a small quantity of a heavy gas still remained; and to this gas the name Argon was given. Since that time it has been found that three other gases of like chemical nature with argon are also mixed with atmospheric nitrogen. These have been separated, and have been named Krypton, Neon, and Xenon respectively.

Recent researches made by Ramsay and Moore[1] seem to indicate that it is extremely unlikely that any other inactive gases of higher atomic weight than xenon exist in the air, unless indeed they should prove to be of a very unstable nature, like the emanations given off by thorium, etc., which may even decompose during the separation processes.

The element helium is also contained in the atmosphere

[1] *Proc. Roy. Soc.*, Aug. 1908.

in extremely minute proportions. It must be understood that the actual amount of any of these inert gases in the atmosphere is very small; argon, by far the most plentiful, only representing about one volume in 107 volumes of air. On account of their marked inactivity it has not been possible to obtain the atomic weights of these gases by the examination of their compounds, for, so far as is known, no such compounds exist. It is true that helium may be regarded as somewhat doubtful in this respect. Certain substances, when they unite together to form compounds, absorb heat while performing this operation, although as a general rule heat is evolved when compounds are formed. Hence it follows that should one of these exceptional compounds (known as endothermic compounds) be decomposed, heat must be liberated at the instant the decomposition takes place. Helium is contained in the mineral fergusonite, and this mineral turns white hot when the helium is being evolved. This would seem to imply, that helium is in combination while it forms a constituent of fergusonite. Still it has not yet been found possible to make any member of this group enter into combination with any other element. Another method must then be adopted in order to ascertain the atomic weights of the gases belonging to this group.

The method employed depends upon the difference which is known to exist between the specific heat of a gas when kept at constant pressure, and that of the gas when the volume remains constant. Heat given

to a gas, the volume of which is kept constant, may be used up in three different ways; (*a*) the molecules of the gas may increase their velocity, so that an increase in the kinetic energy of the gas is brought about, and hence a rise occurs in its temperature; (*b*) the molecules themselves, being composed as a rule of two or more atoms, an amount of relative motion may be imparted to these constituent atoms, and then of course it will necessarily follow that the greater the number of atoms contained in the molecule, the greater will be the amount of heat which will be appropriated for this purpose; and (*c*) it is now known that the atom is not as it was at one time thought to be, an indivisible whole, but is itself built up of simpler constituents. Hence a very small amount of the heat absorbed by the gas may be used up in bringing about changes in the relative movements of parts of the atoms.

When the gas which is being heated is at the same time allowed to expand, that is, it is kept at constant pressure, some additional energy is required to enable the gas to perform external work in overcoming the pressure of the atmosphere through a small distance.

The ratio of the heat absorbed in the two instances may be stated as follows :—

$$\frac{\text{Specific Heat at Constant Pressure}}{\text{Specific Heat at Constant Volume}} = \frac{\text{Increase in Kinetic Energy (Temperature)} + \text{Increase of Atomic Energy} + \text{Energy for Overcoming Pressure}}{\text{Increase of Kinetic Energy (Temperature)} + \text{Increase of Atomic Energy}}$$

Now when the increase in the atomic energy approaches

zero, as it should when the gas experimented upon is monatomic, the value of this ratio becomes 1,66... The larger the amount of absorbed energy which is made use of in bringing about relative atomic movements, the smaller this ratio becomes. Thus, for air and diatomic gases its value approximates to 1·41, but in the case of ether, which has the composition $C_4H_{10}O$, and the molecule of which therefore contains fifteen atoms, the value is only just above unity, viz., 1·05.

If this ratio can be found for these inert gases it can be ascertained whether they are monatomic, diatomic, etc.; and then when this is known, their atomic weights can be found by finding their density as compared with that of hydrogen.

Now Newton was the first to state that the velocity of sound in air could be found from the formula $\text{Velocity} = \sqrt{\frac{\text{Elasticity}}{\text{Density}}}$, but the value obtained by this formula, viz., 28,000 cm. per second, is much too small, and the error lies in the fact that the elasticity required for this purpose is not the isothermal, as Newton had supposed, but the adiabatic. This will be readily understood if it be remembered that since sound travels through ordinary air at about 33,000 cm. per second, the time occupied by a compression or expansion in passing over one centimetre is only $\frac{1}{33,000}$ part of a second, and that during such an extremely short time the air will have practically no opportunity of giving up any of the heat gained by its compression, nor of absorbing

any to make up for that lost during its expansion. So that it becomes necessary to substitute for elasticity the adiabatic volume elasticity of the gas, and this can be proved to be equal to the product of the pressure by the ratio of the specific heats. Thus—

If p=pressure, $\gamma=\frac{\text{Specific Heat at Constant Pressure}}{\text{Specific Heat at Constant Volume}}$, d=the density of the gas, and v=velocity of sound.

The velocity of sound through the gas can be calculated from the formula $v=\sqrt{\frac{\gamma p}{d}}$, from which we also obtain the relation $\gamma=\frac{v^2 d}{p}$. It is then apparent that if the density and pressure of a gas is known, and the velocity with which sound can travel through it is observed, the value of 'γ' can be at once calculated. The velocity of sound through a gas can be easily ascertained by an experiment due to Kundt, even in the cases of those gases which are only obtainable in very small quantities.

A very clean dry glass tube LM, which is about 4 feet long and 2 inches diameter, is closed at one end by a tight-fitting cork M, through which passes a rod OP of wood, glass or metal, the middle of the rod being at M. The stopper at L is made to slide in and out of the

tube, so that the distance between L and P (which is a light disc of wood fastened to the rod O) can be adjusted. A suitable arrangement can be attached for exhausting the tube and also for filling it with the necessary gases in the usual manner. The whole apparatus is firmly clamped to a bench. When the rod O is rubbed by a cloth dusted with resin, longitudinal stationary undulations are set up in it, the middle being a node and the ends antinodes, although the end P acts as a node with reference to the gas in the space LP. Now if a small quantity of lycopodium powder has been placed in the tube between L and P it will be seen when L has been properly adjusted that it is possible to make the lycopodium arrange itself in well-marked ridges, and these ridges will be found to divide the space LP into an exact number of equal parts. The distance between two consecutive ridges may be taken as equal to half a wave-length of the note due to the rod in the gas contained. If other gases are experimented with under similar conditions of temperature and pressure, in the same tube, the relative velocities of sound in these gases can be found by comparing the distance between the nodes for one gas, with those for the others, and so if the absolute velocity in the case of one of the gases, *e.g.* air, is known, that in the case of the others can be found also.

When argon and the other gases of its group are subjected to tests of this description, it is found that the velocity of sound is such, as to justify the assumption

that these gases are monatomic, for the calculated value of 'γ' for all of them approaches 1·66.... Hence their atomic weights must be equal to twice their densities as compared with that of hydrogen.

These gases, as previously mentioned, seem to have no ability for combining with other elements, and may also be looked upon as electrically neutral elements. As such they form an admirable bridge between the most highly negative elements, the halogens, and the most markedly positive elements, those of the alkalies. For this reason they may be placed as suggested in the table in a zero group, then helium (4·0) precedes lithium (7·00); neon (20), sodium (23·00); argon (39·9), potassium (39·10); krypton (81·8), rubidium (85·45); and xenon (128), cæsium (132·81).

Apparently the atomic weight of argon should be slightly less than that observed, in order that it may fit into this position, but the other elements fall into place at once. Now 'γ' as found for argon is 1·659, a quantity slightly less than it should be if argon were a pure monatomic gas. The natural conclusion from this might be that some of the atoms present are in combination with other atoms to form more complex molecules; but the experiment is not of a sufficiently rigid character to be certain in this respect.

An interesting fact with respect to these gases has been noted by Cuthbertson. It depends upon the relative amount by which light is retarded by its passage through the gases and may be briefly stated as follows.

If the amount of retardation due to the passage through air be taken as unity, then that through helium can be represented by 0·124, through neon 0·235, through argon 0·969, through krypton 1·450, and through xenon 2·364. If we let helium $=\frac{1}{2}$, then approximately

neon = 1
argon = 4
krypton = 6
xenon = 10

Series.	Group V.	Group VI.	Group VII.	Group 0.
...	...	...	...	Helium
2	Nitrogen	Oxygen	Fluorine	$139\times1\frac{1}{2}$
	297×1	270×1	192×1	Neon
3	Phosphorus	Sulphur	Chlorine	139×1
	297×4	270×4	192×4	Argon
4	...	...	...	139×4
5	...	...	Bromine	...
			192×6	Krypton
6	...	...	...	139×6
7	...	...	Iodine	...
			192×10	Xenon
8	...	...	...	139×10

If we represent the refractive index by μ, the preceding approximate values which have been observed for the gaseous elements, and those which can be made to assume

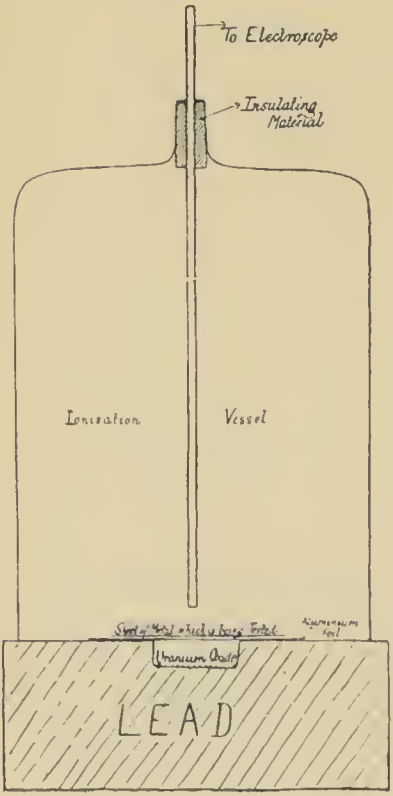
a gaseous form, will represent a value $(\mu-1)10^6$, and may be taken as proportional to the retardation of the light in passing through an equal number of the molecules of the gases mentioned.

This shows how the retardation increases with the atomic weight for elements belonging to the same group, but decreases for an increase of atomic weight for those in the same series, in fact the periodic nature of the variation is at once clearly seen. In this table the elements of group 0 have been considered as a sort of continuation of those in group VII., forming a link between one series and the next.

β-rays, and the Periodic Law.—The absorption which the various elements show for the rays emitted by the radio-active substances, can be used as another illustration of the periodic variations of their properties. In a paper[1] dealing with the absorption of the β-rays from uranium, Crowther gives a diagram which shows this periodic relationship quite distinctly. The β-rays which are emitted by the radio-active substances are negatively charged particles, and are of the same nature as the cathode rays of the vacuum-tube. These rapidly moving negatively charged bodies are able to make a gas such as air, through which they pass, a conductor of electricity, by as it were knocking off negative electrons and leaving the remaining portions of the atoms positively charged. The presence of these rays is made evident in various ways, but it is usual, both when

[1] *Phil. Mag.* (vi.). 12. p. 386.

quantitative, and also when relative measurements are required, to take this conductivity produced in some gas (air most probably) by the passage of these rays, as a measure of the amount of β radiation present. Many of the radio-active substances also emit other rays, and some of these (the α-rays) are also powerful ionisers of the air. These alpha rays, which are positively charged bodies, are much more easily stopped than the β-rays because they travel at a much slower rate. When it is wished to cut off the effect of these rays, a sheet of aluminium foil about 0·1 mm. in thickness is placed as a cover to the substance emitting the rays.



The general arrangement of the radio-active material and the screens is shown in the diagram.

The cavity in the lead, containing the uranium oxide, is completely closed by the aluminium foil, and the lead then forms the floor of the chamber containing the gas, the conductivity of which it is required to measure. For his experiments, Crowther obtained the

metal whenever it was possible to do so as a thin foil, but in some cases this could not be done, and then the element was used in the form of a powder. The powder was then of course arranged in a layer of suitable thickness. If I_0 be taken as a measure of the initial radiation emitted by any radio-active substance, it has been proved experimentally that when this radiation passes through any substance its intensity diminishes according to an exponential law, and that the intensity I at any instant after passing through a thickness 'd' is given by the formula $I=I_0e^{-\lambda d}$. The symbol λ is taken as the coefficient of absorption. Crowther plotted $\frac{\lambda}{\rho}$, where ρ represents the density of the absorbing material, as ordinates, and the atomic weights as abscissæ, and so obtained results such as are shown in the diagram. It will be noticed that the metals of the alkalies and alkaline earths are situated at the commencement of the curves, while those of group VIII. are on the ascending branches near the minima.

M'Clelland and Hackett [1] pointed out also, that the coefficient of absorption as often measured depends upon the quantity of secondary radiation emitted by successive layers of the absorbing material. If the true coefficients of absorption (*i.e.* as they would be if there were no secondary effects) divided by the density of the absorbing substance are plotted against the atomic weights,

[1] *Roy. Dublin Soc. Trans.*, 9, 4, pp. 37-50, March 1907.

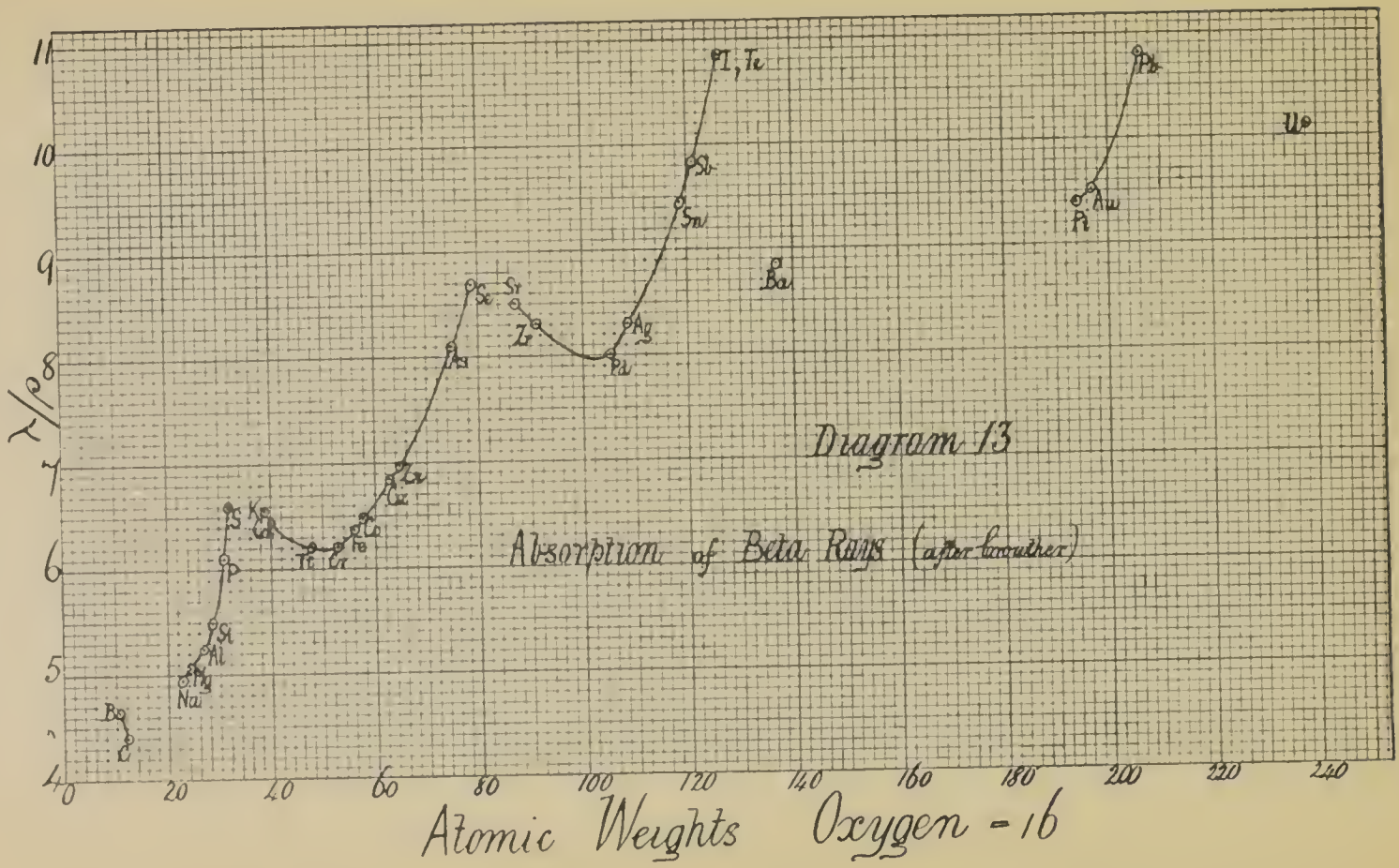
the elements fall into divisions corresponding to the periods of Mendeléeff's table.

The Atomic Weights of Nickel and Cobalt.—A large amount of research has been carried out during the past few years dealing with the relative absorption which takes place when Röntgen rays are made to pass through various elementary substances, and likewise on the Secondary rays [1] which are emitted by different elements when they are bombarded by Röntgen rays. The interest from the point of view of the present subject, centres about the anomaly which is usually presented by the element nickel in such experiments. It will be remembered that for ordinary purposes the same number (59) is used to denote the atomic weights of both cobalt and nickel, and when any distinction is made, that of cobalt is always placed the higher. This is so, since such has always been the result obtained when the atomic weights have been determined by ordinary chemical means.

Now nickel more nearly approaches copper in general properties, than it does iron ; while cobalt on the other hand is more closely allied to iron than copper. As this is the case, according to the Periodic Law the atomic weight of nickel should more nearly approach that of copper, while cobalt's should be closer in value to that of iron, that is, the atomic weight of nickel should be greater than that of cobalt.

When the results of experiments in which the genera

[1] Barkla and Sadler, *Phil. Mag.*, Sept. 1907.


λ/ρ
Tl, Ir
Pb
U
Ba
Sb
Sn
Ag
Pd
Pt
Au
Sr
Zr
Se
Mo
Cu
Ni
Co
Fe
Mn
Cr
V
Ti
Ca
K
S
P
Si
Al
Mg
Na
Be
Li
Diagram 13
Absorption of Beta Rays (after Eve and Mather)
Atomic Weights Oxygen = 16

penetrating power of the Secondary Röntgen rays emitted by the elements is shown by means of a curve obtained by plotting the atomic weights of the elements which give out the rays, as abscissæ, and the penetrating power of these rays for any particular substance as ordinates, nickel can only be made to fit on the curve if an atomic weight of 61·4 is given to it.[1]

Again Sir J. J. Thomson has shown that the kind of curve produced, when the atomic weights of the elements are plotted against their absorption of the Röntgen rays is a smooth one with no marked irregularities except in the case of nickel, and here also uniformity is produced by assuming 61·4 as the atomic weight of nickel; and the same has been shown by Benoist.[2]

It has also been ascertained, that the secondary radiations emitted by any element when subjected to the action of Röntgen rays, are especially penetrating to that element, and the penetrating power for any other element depends upon the nearness of its atomic weight to that of the element giving out the radiation. Thus the radiations given out by copper can most easily pass through copper, but they can also most readily pass through both nickel and cobalt, as their atomic weights are relatively close to that of copper, but still more readily through nickel than cobalt; on the other hand the radiations given out by iron can more easily pass through cobalt than nickel.

[1] Barkla and Sadler (*loc. cit.*).

[2] *Journal de Physique* [3] (x.), p. 659, 1901.

If these results are to be accepted, then the atomic weight of nickel must be slightly increased, or that of cobalt slightly decreased, in order to fit the case; and the positions then occupied by these elements in the table of atomic weights would be in accordance with the Periodic Law. Quite recently, Kaye,[1] working with primary Röntgen rays after they had passed through aluminium screens of thickness greater than 2 mm., found very little change in the relative amounts of radiation from the different metals which he used as anti-cathodes, when the thickness of the aluminium screen was slightly changed. Hence in each case he must have been dealing with beams of hard rays of similar constitution, and it was reasonable to expect that the intensity of the escaping radiations should bear some definite relation to the atomic weights of the elements producing them. In these experiments he found that nickel took up a position justifying 58·7 as its atomic weight. When working with thin aluminium screens, and so in all probability heterogeneous rays, he obtained from the results of the absorption which took place when using screens of iron, nickel, and copper, 61,4 as the atomic weight of nickel. In Barkla and Sadler's work upon the Secondary Röntgen rays from iron, cobalt, nickel, copper and zinc, they plotted the percentage absorptions against the atomic weights of the radiators, and joined the points so obtained for the same screen by a smooth curve, but they assumed that the

[1] *Phil. Trans.*, A 446, 1908.

rays were homogeneous, although at the same time they admitted that this was doubtful.

Further, Dewar and Jones found[1] by means of the vapour density of nickel carbonyl, 58·7 for the atomic weight of nickel. This would make it appear, since various periodic properties point to the atomic weight of nickel being higher than that of cobalt, that this must be arranged by lowering that of cobalt. Such a change may perhaps be ultimately made, for the atomic weight of cobalt is by no means so definitely settled as that of nickel. Parker and Sexton[2] have tried to obtain the atomic weight of cobalt by electrolytic means, comparing it directly with silver for this purpose. The mean result of 15 observations gave a value 57·7, but further work upon this question is needed before it can be regarded as solved, although Mendeléeff was of the opinion that cobalt should be placed before nickel and have an atomic weight less than 59. The values given in the 1909 list of atomic weights are 58·97 for cobalt, and 58·68 for nickel, a difference on the wrong side of 0·29.

Elements of Zero Group of Atomic Weight less than 4. —Mendeléeff[3] has introduced by extra-polation two new elements in the zero group, of less atomic weight than helium. To do this it is of course necessary to have a zero series, and one of the two elements would then

[1] *Proc. Roy. Soc.* A 80, p. 234, 1908.

[2] *Nature*, 76, p. 316, Aug. 1907.

[3] A full account of Mendeléeff's views is given in "Mendeléeff's Chemistry," English edition, Longmans, 1905.

occupy a position in group 0 similar to that at present occupied by hydrogen in group I., as is shown in the accompanying diagram.

...	Group 0.	Group 1.
Series 0.	x	...
Series 1.	y	H
Series 2.	He	Li

In order to find the probable atomic weight of y, use is made of the fact that the ratio of the atomic weights of the elements in series 3 to those in series 2 gradually increases from group VII. to the first group, and that the variation is most rapid in the lower groups. Thus—

$\frac{\text{Chlorine At. Wt.}}{\text{Fluorine At. Wt}} = \frac{35{\cdot}45}{19} = 1{\cdot}86$; $\frac{\text{At. Wt. of Phosphorus}}{\text{At. Wt. of Nitrogen}} = \frac{31}{14} = 2{\cdot}21$; $\frac{\text{At. Wt. of Magnesium}}{\text{At. Wt. of Beryllium}} = \frac{24{\cdot}36}{9{\cdot}1} = 2{\cdot}67$; and $\frac{\text{At. Wt. of Sodium}}{\text{At. Wt. of Lithium}} = \frac{23{\cdot}05}{7{\cdot}03} = 3{\cdot}28$. Then again the ratio $\frac{\text{At. Wt. of Lithium}}{\text{At. Wt. of Hydrogen}} = 7$, and it would therefore be quite natural to suppose that $\frac{\text{At. Wt. of Helium}}{\text{At. Wt. of } y}$ should be greater than 7. On the supposition that this ratio is equal to 10, the atomic weight of 'y' would be 0·4. This, Mendeléeff suggested, may be found to correspond with the substance coronium, which is supposed to exist

in the sun's corona. There is spectroscopic evidence which tends to prove that coronium has a less atomic weight than hydrogen, for the lines due to its presence in the gases surrounding the sun, can be observed at a greater distance from the sun than the lines due to hydrogen.

This element, however, has not yet been discovered on the earth.

Mendeléeff conceived the ether to be a gas with an extremely low atomic weight, and probably to occupy the position in the periodic table as shown by x. Not being an adherent to the theory that all the elements contain some common constituent, he did not conjecture that the other elements were formed from this hypothetical 'x.' However, he thought of 'x' as the most mobile gas, having not only the least atomic weight of all the elements, but also the least density. Belonging as it does to the zero group, it would necessarily be an inert gas similar to the other gases of that group, and so from its position it would be the most inert of all elements. From the isolated nature of its position it is apparent that its atomic weight cannot be arrived at in the same manner as that indicated for 'y,' but, by comparing the ratios of the atomic weights of the other members of the same group, a maximum value 0·17 is arrived at for the atomic weight of 'x.' If this substance 'x' is to be considered as the all-pervading ether, its density must be very much smaller than that of hydrogen, so small in fact, that the motion of its

molecules may be sufficiently rapid to enable it not only to overcome the attraction of the earth, but also that of much larger masses such as the sun and the stars. Making use of the kinetic theory of gases it can be shown that the speed of the molecules of a gas can be calculated from the simple formula $pv = \frac{MV^2}{3}$, in which

p = pressure in dynes per sq. centimetre,
v = volume of the gas in cubic centimetres,
m = mass of gas in grams,
V^2 = average value of squares of velocity of molecules of the gas in centimetres per second.

In the case of hydrogen gas this speed at 0° C. and 760 mm. of mercury pressure, is found to be about 184,000 centimetres per second. To find the velocity of the molecules of any other gas under similar conditions of temperature and pressure, all that is necessary is to divide this quantity by the square root of the density of the gas. Thus assuming x to be monatomic, its density will be $\frac{x\ (\text{Atomic Weight})}{2}$, and the velocity of its molecules will be equal to $184{,}000\sqrt{\frac{2}{x}}$ centimetres per second. Since the velocity will change with change of temperature, increasing with a rise, and decreasing with a fall, it becomes necessary to introduce as a factor $\sqrt{1 + \alpha t}$ (where α is the coefficient of expansion of the

gas and 't' the temperature) to allow for this. It must be remembered in dealing with this question, that the temperature of space is always recognized to be very much below 0° C., but how low it actually is, has not been decided. On this account 'x' must have a much less atomic weight than that given above, or its molecular motion would be altogether insufficient to enable it to escape freely, even from the field of our earth's attraction. In fact, to do this its atomic weight ought to be less than 0·038, while to escape from the sun's attraction it must have an atomic weight less than 0·000013. From arguments of this kind Mendeléeff deduced that in order to escape freely from the attraction of the sun and stars, etc., and so to be able to permeate all space, the atoms of the substance 'x' must have a mass about equal to one-millionth that of the hydrogen atom, and that its molecules must move at the rate of 2250 kilometres per second.

Such a substance as this, would of course not become apparent to us by ordinary physical or chemical means, as the velocity of its molecules would enable them to escape at all times from our grasp, and no containing vessel could be found in which to confine the gas.

Besides imagining these two elements of less density than hydrogen, Mendeléeff spoke in his latest work of a probable new element in the series:—mercury, lead, bismuth in position group VI. series II. This element would thus be the analogue of tellurium, and so he described it under the name Dvi-tellurium (Dt). He further

said that its atomic weight should be about 212, and its oxide should be represented by the formula DtO_3. In a free state the element should be an easily fusible, crystalline, non-volatile metal, of a grey colour, having a density of about 9·3. It should be able to form an oxide DtO_2 which should possess both feeble acid, and also feeble basic properties. When oxidised still further, this oxide should change to DtO_3, which should have properties of a nature similar to those of PbO_2 and Bi_2O_5. The compounds of Dt should be easily reducible, and the metal itself should readily form alloys with the other metals. No such element has yet been discovered, but it is too early to say that Mendeléeff's prophecy will not be fulfilled.

CHAPTER VIII

FORMULÆ TO EXPRESS THE RELATIONSHIP BETWEEN THE ATOMIC WEIGHTS

Several attempts have been made to find a general equation from which the atomic weights of all the known elements might be calculated. Some of these have yielded results, which, considering the nature of the question, may be looked upon as close approximations to the observed values.

If, however, we accept a certain definite atomic weight for each element, then it is clearly impossible to represent these atomic weights by any continuous function, since they are separated by such well-marked gaps.

Dr E. J. Mills [1] was one of the first to turn his attention to the consideration of this branch of the subject.

He proposed a general formula of the type $y=np-n\left(\frac{n}{n+1}\right)^x$. In order to apply this, he divided the elements into sixteen groups. The value of 'np' was different for each one of the groups. It was found that the most suitable value for 'n' was 15; so substituting this for 'n' in the original formula the equation becomes

[1] *Phil. Mag.* (5), 18, pp. 393 *et seq.*, 1884.

$y=15p-15\left(\frac{15}{16}\right)^x$ or $y=15p-15(\cdot9375)^x$. The value of 'x' varies for different members of the same group, but it always increases with an increase in the atomic weight. The quantity 'p' was the same as the number of the group in which the element concerned was placed, and so varied from one to sixteen.

The following are the groups into which Mills divided the elements, and the atomic weights calculated by means of his formula. The accepted atomic weights are also given, so that the comparison between calculated and experimental results may be readily made.

GROUP I

$y=15-15(\cdot9375)^x$

Element.	x	Calculated Atomic Weight.	Observed Atomic Weight, H=1.
Lithium	10	7·13	6·94
Beryllium	14	8·92	9·03
Boron	20	10·87	10·91
Carbon	25	12·01	11·90
Nitrogen	42	14	13·9

GROUP II

$y=30-15(\cdot9375)^x$

Oxygen	1	15·94	15·88
Fluorine	5	19·14	18·84
Sodium	12	23·09	22·81
Magnesium	15	24·30	24·12
Aluminium	25	27·01	26·88
Silicon	32	28·10	28·07

GROUP III

$y=45-15(\cdot9375)^x$

Element.	x	Calculated Atomic Weight.	Observed Atomic Weight, H=1
Phosphorus	1	30·94	30·75
Sulphur	2	31·82	31·81
Chlorine	7	35·45	35·18
Potassium	14	38·92	38·79
Calcium	17	39·99	39·77
Scandium	42	44·10	43·75

GROUP IV

$y=60-15(\cdot9375x)$

Titanium	6	49·82	47·72
Vanadium	8	51·05	50·79
Chromium	10	52·13	51·69
Manganese	17	54·99	54·49
Iron	20	55·87	55·41
Nickel	31	57·97	58·21
Cobalt	41	58·94	58·50

GROUP V

$y = 75 - 15(\cdot 9375)^x$

Element.	x	Calculated Atomic Weight.	Observed Atomic Weight. H=1.
Copper	4	63·41	63·09
Zinc	6	64·82	64·85
Gallium	17	69·99	69·35
Arsenic	Inf.	75·00	74·4

GROUP VI

$y = 90 - 15(\cdot 9375)^x$

Selenium	5	79·14	78·57
Bromine	6	79·82	79·29
Rubidium	18	85·31	84·77
Strontium	27	87·37	86·90
Yttrium	41	88·94	88·3
Zirconium	49	89·36	89·88

GROUP VII

$y = 105 - 15(\cdot 9375)^x$

Niobium	5	94·14	92·76
Molybdenum	7	95·45	95·24
Rhodium	42	104·00	102·18
Ruthenium	46	104·43	100·89

GROUP VIII

$y = 120 - 15(\cdot 9375)^x$

Palladium	1	105·94	105·85
Silver	3	107·64	107·02
Cadmium	9	111·61	111·51
Indium	13	113·52	113·89
Terbium D.	14	113·92	..
Tin	29	117·69	118·06
Antimony	Inf.	120·00	119·25

GROUP IX

$y = 135 - 15(\cdot 9375)^x$

Iodine	9	126·51	125·91
Tellurium	12	128·09	126·49
Cæsium	28	132·54	131·76

GROUP X

$y = 150 - 15(\cdot 9375)^x$

Element.	x	Calculated Atomic Weight.	Observed Atomic Weight. H=1.
Barium	2	136·82	136·28
Lanthanum	5	139·14	137·8
Cerium	9	141·61	139·14
Didymium	18	145·31	..

GROUP XI

$y = 165 - 15(\cdot 9375)^x$

Samarium	1	150·94	149·21

GROUP XII

$y = 180 - 15(\cdot 9375)^x$

Erbium	1	165·94	166·07
Ytterbium	12	173·09	170·64

GROUP XIII

$y = 195 - 15(\cdot 9375)^x$

Tantalum	2	181·82	179·56
Tungsten	4	183·41	182·54
Iridium	28	192·54	191·57
Platinum	50	194·40	193·45

GROUP XIV

$y = 210 - 15(\cdot 9375)^x$

Gold	1	195·94	195·64
Osmium	?	..	..
Mercury	6	199·82	198·41
Thallium	13	203·52	202·48
Lead	22	206·37	205·46
Bismuth	28	207·54	206·35

GROUP XV

$y = 225 - 15(\cdot 9375)^x$

N	14	218·92	..

GROUP XVI

$y = 240 - 15(\cdot 9375)^x$

Thorium	10	232·13	230·58
Uranium	Inf.	240	236 61

From the very nature of the equation it is at once apparent that the atomic weights calculated therefrom can only be whole numbers in the exceptional cases in which x has either the value 0 or infinity.

The equation $y=15p-15(\cdot 9375)^x$ suggests that an upper limit to the atomic weights exists, for when 'p' becomes very large, the negative part of the expression will be sufficiently small, in comparison with $15p$, to be neglected.

Again if we consider the values of $15(\cdot 9375)^x$ for all values of x between 0 and infinity, we find that the sum of all possible values of that expression is equivalent to $\frac{15}{1-\frac{15}{16}}=240$. This is a very remarkable coincidence with the then accepted atomic weight of uranium, the element possessing the greatest atomic weight of all the known elements.

In order to bring hydrogen into line with the other elements, Dr Mills imagined it to be a survival of some earlier changes in the elements, and he suggested two other groups which should form a separate series.

Thus, adapting the general formula $y=pn-n\left(\frac{n}{n+1}\right)^x$ to the two groups of this series, we have atomic weight of hydrogen $=1\times 1-1\left(\frac{1}{1+1}\right)^x$. When x is infinite the value so obtained becomes unity, so that hydrogen would represent the last element of the group to which it belongs. This would imply the possible

existence of elements having a less atomic weight than hydrogen.

In 1890[1] Carnelley attacked this problem, and he suggested the general formula $A = c(m + v^{\frac{1}{x}})$ or $\frac{A}{m + v^{\frac{1}{x}}} = c$.

In this A represents the atomic weight, C is a constant, m is a member of the progression $2\frac{1}{2}$, 5, $8\frac{1}{2}$, then by increments of $3\frac{1}{2}$ to 33, v is the maximum valency, or in other words the number of the group of Mendeléeff's table in which the element occurs.

He also found that the best value for x was 2, so that the equation is thus reduced to the form $A = c(m + \sqrt{v})$.

The values of C calculated by him from the atomic weights of 55 elements all lie between 6·0, the value obtained for carbon, and 7·2, that obtained for selenium. The mean value for the whole 55 is 6·64. The higher values for C occur chiefly in the cases of those elements belonging to groups V., VI. and VII. While the lower values are obtained for elements of groups I., II., III. and IV. In the following table are given the values obtained for C, and the atomic weights from which he calculated those values.

The series into which the elements have been divided are the same as those of Mendeléeff's table.

[1] Carnelley, *Phil. Mag.* (v.), 29, 1890, pp. 97 *et seq.*

Even Series

Series II., $m=0$.

	Atomic Weight when H=1	Calculated value of $\frac{C \text{ or } A}{m+\sqrt{r}}$
Lithium	7	7·0
Beryllium	9·1	6·45
Boron	10·9	6·30
Carbon	12·0	6·0
Nitrogen	14·0	6·25
Oxygen	16·0	6·53
Fluorine	18·9	7·13
Mean . .		6·52

Series IV., $m=5$

Potassium	39·0	6·50
Calcium	40	6·24
Scandium	44	6·54
Titanium	48	6·86
Vanadium	51·3	7·09
Chromium	52·0	6·98
Manganese	54·0	7·06
Mean . .		6·75

Series VI., $m=12$.

Rubidium	85·3	6·56
Strontium	87·4	6·52
Yttrium	89·8	6·54
Zirconium	90·4	6·46
Niobium	94	6·60
Molybdenum	95·5	6·61
Mean . .		6·55

Series VIII., $m=19$.

Cæsium	132·6	6·61
Barium	136·8	6·70
Lanthanum	138·0	6·66
Cerium	139·9	6·66
Didymium	142·0	6·69
Mean . .		6·66

Odd Series

Series III., $m=2\frac{1}{2}$.

	Atomic Weight when H=1.	Calculated value of $\frac{C \text{ or } A}{m+\sqrt{r}}$
Sodium	23	6·57
Magnesium	24·4	6·24
Aluminium	27·0	6·38
Silicon	28·3	6·29
Phosphorus	31·0	6·54
Sulphur	32·0	6·46
Chlorine	35·4	6·87
Mean . .		6·48

Series V., $m=8\frac{1}{2}$.

Copper	6·33	6·66
Zinc	65·3	6·59
Gallium	68·9	6·73
Germanium	72·3	6·88
Arsenic	74·9	6·97
Selenium	78·8	7·20
Bromine	79·8	7·16
Mean . .		6·88

Series VII., $m=15\frac{1}{2}$.

Silver	107·7	6·54
Cadmium	111·8	6·61
Indium	113·4	6·58
Tin	117·7	6·72
Antimony	119·6	6·74
Tellurium	125·0	6·96
Iodine	126·5	6·97
Mean . .		6·73

Series IX., $m=22\frac{1}{2}$, *wanting.*

Even Series		
Series X., $m=26$.		
	Atomic Weight when H=1.	Calculated value of $\frac{C \text{ or } A}{m+\sqrt{v}}$.
Tantalum	182·1	6·45
Tungsten	183·6	6·45
Mean . .		6·45
Series XII., $m=33$.		
Thorium	231·9	6·62
Uranium	238·5	6·72
Mean . .		6·67

Odd Series		
Series XI., $m=29\frac{1}{2}$.		
	Atomic Weight when H=1.	Calculated value of $\frac{C \text{ or } A}{m+\sqrt{r}}$.
Gold	196·9	6·46
Mercury	199·7	6·46
Thallium	203·7	6·52
Lead	206·5	6·56
Bismuth	208·2	6·56
Mean . .		6·51

N.B.—The atomic weights and values are here as given by Carnelley.

For group VIII. of the periodic table a separate arrangement was found necessary in which 'v' was taken to represent the numerical order of the element in the series to which it belongs.

Thus :—

M=5.	C	M=12.	C	M=19.	C	M=26.	C	Values of 'r.'
Iron	7·14	Rubidium	6·98	...	...	Osmium	6·69	8
Cobalt	7·34	Rhodium	6·94	Wanting	...	Iridium	6·64	9
Nickel	7·18	Palladium	7·00	...	...	Platinum	6·66	10

When the formula $A=c(m+\sqrt{v})$ was used for calculating the atomic weights of the elements, it was

found when C was represented by its average value 6·64, that the mean error for 54 elements was only ± 1·9. On the other hand Carnelley stated that when 6·4 is taken as the average atomic heat of the elements, and Dulong and Petit's law is made use of in the calculation of the atomic weights, the average error amounts to as much as ± 4·2, even if we exclude all those elements (carbon, silicon, boron, nitrogen, oxygen, fluorine and hydrogen) which have abnormal atomic heats.

The average value of C (6·64) is so near the average value obtained for the atomic heats (6·4), that Carnelley was tempted to consider them to represent the same thing.

Then we have atomic heat $\times(m+\sqrt{v})$=atomic weight; or atomic weight=(atomic weight)$\times$(specific heat)$\times$ $(m+\sqrt{v})$, from which the relation specific heat= $\frac{1}{m+\sqrt{v}}$ is at once obtained.

Carnelley used this equation for calculating the specific heats of 55 of the elements, and in 45 cases he found that the calculated values agreed with those obtained by experiment. The remaining 10 elements were those, the specific heats of which are abnormal according to the law of Dulong and Petit.

Later still Dr J. H. Vincent [1] has proposed a formula to include 58 of the elements. His formula is $W=(n+2)^{1\cdot21}$ in which W represents the atomic weight of the element, n represents the numbers from 3 to 60 inclusive. The number 1·21 is obtained as follows.

[1] *Phil. Mag.* (6), 4,, pp. 103 *et seq.*

Suppose $W=N^q$ where $N=n+2$,

then $\log W = q \log N$,

therefore $q=\frac{\Sigma \log W}{\Sigma \log N}=1{\cdot}21$.

This formula was applied by him to calculate the atomic weights of the elements from lithium ($n=3$) to samarium ($n=60$); the elements for this purpose being arranged in order of their atomic weights, the value of 'n' being increased by unity for each successive element.

The mean difference between the calculated and observed atomic weights for the 58 elements amounted to only 1·01, and as was the case with Carnelley's formula, several of those showing the greatest amount of deviation are among the exceptions to Dulong and Petit's law.

Besides this he prepared what he called an "augmented list" to include all the known elements.

The following list will show the positions of the remainder of the elements the atomic weight of which exceeds that of samarium, and also the connection of these elements with those of lower atomic weight, so far as this formula is concerned.

	Element.	N.		Element.	N.
	Hydrogen .	1		From this to Samarium	
	..... .	..		$N=(n+2)$	
	Helium .	3	$n=60$	Samarium .	62
	..... .	..		....	..
$n=3$	Lithium .	5		....	..

Element.	N.	Element.	N.
Gadolinium .	65	Gold . .	79
Terbium . .	66	Mercury . .	80
....	. .	Thallium . .	81
Erbium . .	68	Lead . .	82
....	..	Bismuth . .	83
Thulium . .	70	....	84
Ytterbium .	71	....	85
....	..	....	86
Tantalum . .	73	....	87
Tungsten . .	74	....	88
....	. .	....	89
Osmium . .	76	Thorium . .	90
Iridium . .	77	....	91
Platinum . .	78	Uranium . .	92

Using this augmented list it becomes possible to calculate the atomic weights of all the elements from one general formula $W=(N)^{1.21}$.

The dotted lines represent gaps which it has been necessary to leave in order that N may have the proper magnitude, for the calculated and observed results to agree. Yet, as he points out, these gaps are not excessive, for while only two such gaps occur between samarium and gadolinium there are 5 vacant spaces between these two in the periodic table if we include 3 probable elements in group VIII.

Europium now fills one of the vacant spaces between gadolinium and samarium, while dysprosium fills the gap

between terbium and erbium, and lutetium that between ytterbium and tantalum.

It will also be noted that this table allows of one new element between hydrogen and helium and another between helium and lithium.

As to the probable total number of elements, while this formula would suggest a lower limit (hydrogen), no upper limit is necessary.

In 1907 M. Minet[1] brought forward a formula for connecting the atomic weights of the elements, which in some respects is only a modified form of that suggested by Vincent. He plotted a curve in which the abscissæ were the numbers corresponding to the elements, when these are arranged in a series in the ascending order of their atomic weights (thus in this series hydrogen is represented by 1 and uranium by 79); the ordinates were the atomic weights of the elements.

The curve formed by joining all the points so obtained consists of two parts, a small first part comprising all the elements between the values $x=2$ (*i.e.* helium) and $x=20$ (*i.e.* calcium), in which the points lie along a straight line; and a larger second part including hydrogen, and all the elements between $x=20$ (calcium) and $x=79$ (uranium), in which the curve joining the points is a parabola. The two parts of the curve cut at $x=20$. The first part of the curve is represented by the equation $y=1{\cdot}985x$, while the equation which represents the parabolic portion is $y=x^{1{\cdot}23}$. The differ-

[1] *C. R.*, 144, 8, 1907.

ences between the atomic weights as calculated from these formulæ, and those obtained by experiment, range from 1 to 3 per cent. of the observed values; this discrepancy increases with increasing atomic weights.

If new elements are included between hydrogen and calcium, such as one between hydrogen and helium and a second between helium and lithium, the two curves would become one, and the atomic weights of the 81 elements can then be represented by the equation $y=x^{1\cdot215}$.

The curve obtained from this equation gives values for the atomic weights, differing from experimental results by amounts, some positive, some negative, which vary from 1 to 3 per cent., except for the elements radium, thorium, and uranium, in which the difference is as great as 10 per cent. In order that these elements may fall into line with the others it becomes necessary to predict four new elements between bismuth and radium and one between radium and thorium, also one more between thorium and uranium, just as suggested by Vincent. The total number of elements having atomic weights between 1 and 240 inclusive, required by M. Minet's formula, is 87, while Vincent's required 92.

Delauney [1] suggests that the atomic weights of the elements, when oxygen=16 is taken as the standard, can be represented by $\frac{A^2}{n}$, where A and n are both whole numbers. Thus :—

[1] *C. R.*, 145, 25.

Helium $= 2^2/_1$ Potassium $=14^2/_5$ Silicon $=16^2/_9$
Mercury $=20^2/_2$ Molybdenum $=24^2/_6$ Arsenic $=30^2/_{12}$
Carbon $= 6^2/_3$ Beryllium $= 8^2/_7$ Bromine $=39^2/_{19}$

and so on. In some cases it happens that analogous bodies have divisors which are equal or nearly so, or else they form a regular progression. Thus :—

Cadmium $=15^2/_2$ Lithium $=13^2/_{24}$ Beryllium $= 8^2/_7$
Mercury $=20^2/_2$ Rubidium $=47^2/_{26}$ Strontium $=35^2/_{14}$
Zinc $=14^2/_3$ Cæsium $=61^2/_{28}$ Barium $=62^2/_{28}$

It also often happens that 'n' is quite different in such cases, and no simple relationship can be established between its values. To get over this difficulty he modified the form of his ratio to $\frac{(Aa)^2}{na^2}$, where 'a' is representative of a whole number. Thus :—

Sodium $=22^2/_{21}$; Potassium $=14^2/_5$, that is $28^2/_{20}$.

Finally he shows by examples of elements belonging to the same family the regularity and symmetry of the values of 'n' in such cases. Thus :—

Fluorine $=19^2/_{19}$, Bromine $=39^2/_{19}$,
Chlorine $=45^2/_{57}$, Iodine $=85^2/_{57}$; and so on.

Surely such attempts as this last can have no intrinsic value, for although by a little mathematical juggling analogous elements can be brought into some sort of connection with one another, no object has been attained by so doing. No new facts are thus brought to light ;

nor does it in any way add to the evidence which already exists as to the similarity of the elements contained in any group. They have been given here to show what has been done in this respect in more recent times.

The same cannot of course be argued against such formulæ as that of Carnelley, in which the constants and variables used in the calculations may be looked upon as representing some physical or chemical properties of the elements, as well as the properties of number, while the groups into which he divides the elements correspond to the series of Mendeléeff's table.

CHAPTER IX

THE ATOM AND THE PERIODIC LAW

Perhaps there is no more fascinating problem in the whole realm of physical chemistry than that which deals with the ultimate structure of the atom, for recent researches have made it quite clear that the atom itself is not the ultimate particle. If we accept the Periodic Law in its entirety it seems to be also essential that we accept some system of development of the elements, which may in some degree help us to account for the periodicity in their properties, such as occurs with certain increases of the atomic weights.

It is by no means necessary to try to develop the whole system of chemical elements from the same ultimate particle, but if we consider the odd or even series of any one group, it would seem that there is some common matter that confers upon the elements which occur with definite increases of atomic weight, such extraordinary similarity in their characteristic properties. In other words we might assume some structure or matter, or, it may be both, which is common to all the elements of the sub-group, on which the family relationship depends, while some variable quantity might determine

the individual characteristics proper to each element of the group. Lord Kelvin, however, was of the opinion that we could not expect to be able to account for the various chemical elements in this manner. Writing to the *Philosophical Magazine* in September 1907, he said, "Though no doubt some important and interesting differences of quality, such as the difference between ordinary and red phosphorus, are due to the differences of grouping in assemblages of one kind of atom, it seems extremely improbable that differences of grouping of atoms all equal and similar, suffice to explain all the different chemical and other properties of the chemical elements. It seems indeed almost absolutely certain that there are many different kinds of atom each eternally invariable in its own specific quality, so that no element is capable of being transmuted into any other." Yet various theories as to the probable common ultimate constituent of the atoms of all the elements have from time to time been brought forward, for even although that portion of the atomic theory which claims that the atom is the smallest portion of matter to enter into a compound had been generally accepted, yet from the time of Prout onwards there have always been those who have clung to the idea that it was possible to find some constituent common to the atoms of all elements, in fact that the elements are after all only modified forms of one and the same material.

During the last few years the researches on the conductivity of electricity through gases, and the discovery

of the radio-active substances, have brought to light new facts which have induced many to regard this problem from a slightly different point of view.

It has been proved experimentally that the negatively charged particles known as electrons, which are given off by the radium compounds as the so-called β-rays, and are also met with in the cathode rays of the vacuum tube, etc., possess a mass which is only about $\frac{1}{1800}$th part of the mass of an atom of hydrogen.

Now the question as to the nature of these electrons must necessarily arise. Are they small particles of matter of less size than an atom, or are they as it were disembodied charges of electricity which owe their apparent mass to their very rapid motion. Larmor considers them to represent strain centres in the ether. This question involves the consideration of the much wider one as to the relationship between what is known as matter, and the ether. The general trend of modern thought along these lines is to regard the ether as the all-essential something, and matter as simply to result from modifications in the ethereal structure. A further consideration of this is however beyond the scope of the present book, and those readers who are interested in the subject may refer to works devoted to its study, such as those by Professor Larmor and Sir Oliver Lodge.

It may however be mentioned that Sir J. J. Thomson has made a calculation of the extra inertia which would result from the very rapid movement of such an electron; and Professor Kaufmann has by a series of experiments,

in which he made use of the β-rays emitted by radium, actually measured the increase which takes place in value of the mass of an electron as its velocity is increased.

The close agreement which exits between the calculated values and those found as the result of experiment is shown in the following table :—

Velocity of Electrons in cm. per Second.	Ratio of the Mass at Velocity stated to the Mass of a slowly moving Electron.	
	Calculated by Sir J. J. Thomson.	Observed by Professor Kaufmann.
$2{\cdot}36\times10^{10}$	1·65	1·5
$2{\cdot}48\times10^{10}$	1·83	1·66
$2{\cdot}59\times10^{10}$	2·04	2·0
$2{\cdot}72\times10^{10}$	2·43	2·42
$2{\cdot}85\times10^{10}$	3·09	3·1

Such close agreement between the results is surprising, considering the nature of the problem, and it certainly would appear as if we are safe in suggesting that these electrons do not contain matter as we ordinarily know it.

Since the velocity of light is about 3×10^{10} cm. per second, the above table shows that no very decided increase in the mass takes place until the velocity of the electron is an appreciable fraction of that of light, then the increase becomes rapid and would become infinitely great as the velocity of the electron approached that of light.

These negative electrons are not detected under ordinary circumstances except in the case of the radio-active elements. Yet one is naturally inclined to wonder whether radio-activity is not a property common to all matter, but that in the great majority of elements we are unable to detect it simply because of the want of more delicate instruments. Campbell [1] has recently found that potassium compounds give off rays which he considers exhibit characteristics similar to the β-rays given off by uranium X, one of the products formed by the degeneration of uranium. The penetrating power of these β-rays from potassium is not quite so great as that of the β-rays emitted by uranium X. The other elements of the alkali group were also examined at the same time, and rubidium, alum, and cæsium chloride exhibited the property of radio-activity in a slight degree. It has likewise been known for some years, that metals when exposed to the action of ultra-violet light have the power to emit negatively charged corpuscles. The most active in this respect are the most highly electro-positive metals, such as rubidium, potassium, and sodium; an alloy of sodium and potassium which is a liquid at ordinary temperatures can also be used as a source of these negative electrons. Professor Fleming, at a meeting of the Physical Society, November 1908,[2] showed an experiment in which an electric cell was produced by using this alloy as one pole, and the current in

[1] *Phil. Mag.* (6). 93, Sept. 1908.
[2] *Phil. Mag.*, 17, pp. 286-295, 1909.

the cell was produced by the electrons set free when this pole was brightly illuminated by means of an arc lamp.

The alloy was contained in a vacuum tube and the other pole of the cell was a piece of platinum also in the tube. When the alloy was illuminated the negative electrons emitted by it carried a negative charge to the platinum plate, and while the illumination continued, quite a large deflection was obtained on the galvanometer placed in series.

He also showed that the light which had the greatest amount of influence was of the same wave-length as that which the substances would emit if raised to incandescence.

Sir J. J. Thomson[1] and also Lenard[2] have shown that the ratio $\frac{e}{m}$ (where 'e' represents the charge carried by these electrons and 'm' their mass), is the same for these electrons as for those emitted by radio-active substances, etc. The same has also been shown to be true with respect to the negative carriers emitted by incandescent wires.

In the well-known oscillation valve of Professor Fleming the negative electrons given out by the incandescent carbon filament make it possible to transform an alternating into an unidirectional current, or rather to obtain such a current from an alternating source.

Hot lime also emits negatively charged electrons, and

[1] *Phil. Mag.* (5), 48, p. 547, 1899.
[2] *Ann. der Phys.*, ii. p. 359, 1900.

in such enormous quantities, that when a small piece of platinum foil covered with lime, and heated until almost white hot by an independent source of current, is used as the cathode in a vacuum tube, it is possible to cause a discharge to pass through the tube by applying only relatively small potential difference. The experiments of the author [1] dealing with the electrical conductivity produced by heating various chemical compounds, in which the presence of both negatively and positively charged ions was brought about by changes which the heat produced on the chemical compound, all point in the same direction. For although their velocity as then measured tended to show that under these conditions the ions possessed a much greater mass than that of the negative electron, yet it must be borne in mind that the conditions of the experiments were such as to make itquite certain that it was not simpleelectrons which were being examined, but aggregations of matter which had collected round some such charged centre. So that after all the electron was present but in a very much disguised form.

Then suppose we admit for the moment that all matter possesses the power to give off these negatively charged electrons under certain conditions. The enormous velocities with which they travel has already been stated, and we are led to wonder how such a thing is brought about. Are these electrons ejected as the

[1] Garrett and Willows, *Phil. Mag.*, Oct. 1904; Garrett, *Phil. Mag.*, 1907.

result of some kind of atomic explosion to which alone they owe their great speed, or are they already in rapid motion in the atom itself, and has that motion from some cause or other become suddenly accelerated to such an extent that the electron breaks free from its orbit, and escapes from the atom? The second certainly seems to be the more likely explanation for various reasons, one of which is connected with the behaviour of the spectral lines obtained by the analysis of monochromatic light, when the source of light is subjected to the action of strong magnetic fields. This we shall proceed to consider in some detail.

The light emitted by an incandescent solid or liquid mass when analysed by the spectroscope exhibits a continuous spectrum, but light emitted by an incandescent gas when so examined shows only bright lines which occupy definite positions in the spectrum according to the gas used.

Let us suppose that the continuous spectrum is produced when the light examined is the result of collision of atom with atom due to the great temperature and pressure employed; but that with higher temperatures and lower pressures the electrons moving in the atoms are the cause of the light, and not the vibrations of the atom as a whole.

If the lines of the spectrum are produced by the vibration of the electrons in the atom, then since we are here dealing with a moving charge of electricity, there must also be a magnetic field due to this electricity

in motion, and the light is produced by the series of electro-magnetic disturbances thus set up in the ether. Now apply to this another magnetic field and it should be possible to produce a change in the motion of the electron to which the first magnetic field is due.

Faraday foresaw that some such result should take place, but was not able to prove the truth of his theory by experiment owing to the small resolving power of his spectroscope. Necessarily the amount of change in the motion of the electron will be extremely minute, even when very powerful magnetic fields are used, so that it is essential that the instrument used for analysing the light shall be able to separate the individual parts of the spectrum to a great extent in order that any change in the relative positions of the lines, or splitting up of the lines may be visible.

Hence it was not until 1896 that Professor Zeeman of Amsterdam was able while analysing the light given out by incandescent sodium vapour, to broaden somewhat the 'D' lines by subjecting the source of light to the action of a strong magnetic field. By closer investigation he was able to show by this means that the two yellow (D) lines can be split up into several components, and that the light producing these components is polarized in different planes.

Imagine the electrons to be revolving in circular orbits, then the light emitted in directions perpendicular to the plane of their orbits will be circularly polarized.

If now a magnetic field is applied in the direction of propagation of this circularly polarized light, the periods of those revolving electrons producing the light will be altered, since the magnetic fields due to these moving charges will be in the same, or opposite direction, according to the direction of revolution of the electron.

Lorentz has given a mathematical explanation of the change of the orbit of the electron which results when an external magnetic field is applied, and the consequent amount of shift of the lines of the spectrum which might be expected. Briefly stated in a simplified form it is as follows :—

Suppose an electron of mass 'm' and charge 'e' revolving with a velocity v in an orbit of radius 'r' to be subjected to a magnetic field of intensity H ; the direction of the magnetic field to be at right angles to the plane of the orbit of the electron. Then before the magnetic field is applied there is a tendency of the electron to fly off from its orbit which may be indicated by fr, and this is counterbalanced by a force acting toward the centre the magnitude of which is given by $\frac{mv^2}{r}$.

As soon as the magnetic field is applied the electron is subjected to another force, which since it acts in a direction which is at right angles both to the direction of the magnetic field, and also to the direction in which the electron is moving at any instant, must act along

the radius of the electron's orbit. The magnitude of this force is $\frac{Hev}{V^2}$, where V is the velocity of light and H the magnetic field applied.

Let T_1 and r_1 represent the new periodic time and radius of revolution respectively.

$$\text{Then } \frac{mv^2}{r_1} = fr_1 - \frac{Hev}{V^2}; \text{ while } \frac{mv^2}{r} = fr.$$

Subtracting and thus eliminating f we obtain—

$$\frac{mv^2}{r_1^2} - \frac{mv^2}{r^2} = -\frac{Hev}{r_1 V^2};$$

$$\text{but } T = \frac{2\pi r}{v} \text{ and } T_1 = \frac{2\pi r_1}{v}; \text{ so that}$$

$$\frac{1}{T^2} = \frac{v^2}{4\pi^2 r^2} \text{ and } \frac{1}{T_1^2} = \frac{v^2}{4\pi^2 r_1^2};$$

$$\text{thus } \frac{1}{T_1^2} - \frac{1}{T^2} = \frac{v^2(r^2 - r_1^2)}{4\pi^2 r^2 r_1^2}.$$

$$\text{Again } \frac{mv^2}{r_1^2} - \frac{mv^2}{r^2} = \frac{mv^2(r^2 - r_1^2)}{r_1^2 r^2} = -\frac{Hev}{r_1 V^2}.$$

$$\text{Therefore } \frac{1}{T_1^2} - \frac{1}{T^2} = -\frac{Hev}{4\pi^2 m r_1 V^2}, \text{ and by}$$

$$\text{substituting } T_1 \text{ for } \frac{2\pi r_1}{v} \text{ we obtain}$$

$$\frac{1}{T_1^2} - \frac{1}{T^2} = -\frac{He}{2\pi m V^2 T_1}.$$

Since the amount of change of period is always very small, TT_1 may be taken as equal to T^2, and $T + T_1$ as equal to $2T$.

Hence $\frac{1}{T_1^2}-\frac{1}{T^2}=\frac{T^2-T_1^2}{T_1^2T^2}=\frac{2T(T-T_1)}{T^4}=\frac{2(T-T_1)}{T^3}$,

and $T-T_1$, or the difference in the periods,

is given by $-\frac{He\,T^3}{4\pi mV^2T}$, *i.e.* $-\frac{He\,T^2}{4\pi mV^2}$.

If this is taken to apply to the electrons moving in clockwise orbits, then it must be remembered that to apply it to those moving in anticlockwise orbits the sign of $-\frac{He\,v}{V^2}$ must be changed in order to be correct for the same magnetic field.

If the electron is moving in a clockwise direction when this change takes place its period is decreased by $-\frac{He\,T^2}{4\pi mV^2}$, for, as we shall see later, the period is shortened in the case of such an electron.

In diamagnetic bodies the electrons may be considered to be moving in a great many different planes, and the orbits in some cases to be performed in a clockwise manner, and in others in an anticlockwise direction.

Before the application of the magnetic field the periods of these electrons will be the same, but when the field is applied both periods will be changed, and one will now differ from the other by $\frac{He\,T^2}{2\pi mV^2}$, and so the wave-length of the line will be altered. Hence when the spectrum of any source of monochromatic light is viewed in a direction along the lines of the magnetic field, we may expect two lines to appear instead of one. And further,

one line will be circularly polarised in one sense, and the other in the opposite.

In order to carry out this experiment it is necessary to work with a magnet having a hole bored through each pole piece, so that when looking through these two holes the line of sight may be in the same direction as the lines of force due to the magnet.

These accelerated and retarded electrons will send out waves of light in directions parallel to the plane of their orbits as well as at right angles to them. This light given out in a direction parallel to the planes of the orbits of the electrons, and so at right angles to the magnetic field, will be altered in wave-length just in the same way as that viewed in the direction of the field, but the two lines obtained in this manner are plane polarised and would form the outer lines in a normal Zeeman triplet.

Next, suppose the electrons are revolving in planes parallel to the magnetic field, in this case the force acting upon the electron due to the external magnetic field will act in a direction perpendicular to the plane of its orbit.

Such circular orbital motions may all be resolved into two rectangular motions, one in the direction of the magnetic field, and the other in a direction perpendicular to the field and also to the line of propagation of the light, that is, to the direction in which the light is observed.

The period of an electron which is moving in the direction of the magnetic field will remain unaltered by that field, so that in some cases the light emitted will retain its original wave-length and the line will be seen

in the same position as before the field is applied. This line will be polarised in a plane at right angles to the magnetic field.

The periods of the other components whose motion is in planes at right angles to the magnetic field will undergo a change, some being increased and others diminished.

Thus when a source of monochromatic light is subjected to a magnetic field which acts in a direction at right angles to the line of sight, and we analyse the light we may expect to find that the single line has been split up into three distinct components, a central one, which is plane polarised, and occupies the same position in the spectrum as the original line, the plane of polarisation being perpendicular to the direction of the field; and two plane polarised lines whose periods differ by an amount $=\frac{He\,T^2}{2\pi m V^2}$. The wavelength of one of these lines will be greater than that of the original line, while that of the other will be smaller, thus one will appear on either side of the central line. These lines are also plane polarised but in a direction at right angles to that in which the central line is polarised.

In the great majority of cases in which the lines have been examined in the manner indicated, the results are much more complicated than those indicated above, since the latter represent what might be expected to occur in an ideal case. The red line of the calcium spectrum does however split up into three components

when viewed at right angles to the field, and two when in the direction of the field. On the other hand both the well-known yellow (D) lines of sodium behave in an abnormal manner, D_1 resolving into four components instead of three, and D_2 into six instead of three.

It is very difficult to account for these divergencies. Michelson has advanced the opinion that it may be due to the motion of the electrons in the atom, not being a pure harmonic vibration.

It is possible that changes in the motion of any one electron may be affected by the vicinity of other electrons whose motion is being changed. This will produce other perturbations in their orbits, and a further resolution of the lines will result. This effect is known as the Zeeman Effect, that name having been given to it in honour of the physicist who was the first to observe it. By this effect we are led to the conclusion that the electrons which are contained in the atom are in a state of constant activity, and we naturally inquire whether there is any connection between the moving bodies which produce these results, and those β-rays which are emitted by the radio-active substances, which make their presence known to us by the electrical conditions which they set up.

Let us suppose that the period of the electrons revolving in a clockwise direction when the light is viewed along the lines of force due to the magnet is changed from T_o to t, and those of the electrons with anticlockwise motion is changed from T_o to T.

We have already seen that $t-T=\frac{He\,T_o^2}{2\pi m V^2}$.

Let λ=wave-length of the light concerned,

then $\lambda_c=Vt$ and $\lambda_a=VT$.

Also $t-T=\frac{\lambda_c-\lambda_a}{V}$; $T_o^2=\frac{\lambda_o^2}{V^2}$.

So that $\frac{t-T}{T_o^2}=\frac{He}{2\pi m V^2}=\frac{(\lambda_c-\lambda_a)V}{\lambda_o^2}$,

from which $\frac{e}{m}=\frac{(\lambda_c-\lambda_a)V}{H\lambda_o^2}\times(2\pi V^3)$.

All the quantities on the right-hand side of the equation are known, so that by this means it is possible to prove that $\frac{e}{m}$ has the same value for all the elements which have been examined in this manner. Further, the value of $\frac{e}{m}$ can be calculated in absolute units. When this is done for the D_1 line of sodium its value is found to be $5{\cdot}1\times10^{17}$ in electrostatic units.

Assuming 'e' in the same units to be represented by $3{\cdot}4\times10^{-10}$, we find that 'm' must be equal to $\frac{3{\cdot}4}{10^{10}\times5{\cdot}1\times10^{17}}=\frac{2}{3}\times{}^1/_{10^{27}}$ or $\frac{6{\cdot}6}{10^{28}}$.

When calculated from electrolytic data the mass of the hydrogen atom is found to be $\frac{1{\cdot}1}{10^{24}}$. Thus the electron contained in the sodium atom must have only about $\frac{1}{1800}$ the mass of the hydrogen atom, and this has also been

found to be the magnitude of the mass of the negative electrons given off by the radium compounds, etc.

If we can next show that the electrons producing the Zeeman effect are negatively charged, we shall be justified in considering them to be of the same nature as those which we are able to examine in a free state. It has been found experimentally in the case of light examined along the lines of magnetic force, that the circularly polarised line due to the clockwise vibration has a shorter wave-length than the line due to the anti-clockwise vibrating electron.

The difference in period between the two lines is $t_c - T_a = \frac{He\,T_o^2}{2\pi m V^2}$. T_a having been found by experiment to be greater than t_c, $\frac{He\,T_o^2}{2\pi m V^2}$ must therefore be a negative quantity. The only factor which can have a negative sign in this expression is 'e,' hence we must conclude that the electrons producing this effect are negatively charged. Before leaving this point, it may be as well to point out that the amount of separation which takes place is always extremely small. With a very powerful magnetic field the two outer components of the D_1 line of sodium are separated by no more than $\frac{1}{12}$ the distance which the same spectroscope shows between the two yellow lines before the field is applied. The best modern appliances are therefore essential in order that the Zeeman Effect may be observed as described. An effect [1]

[1] Cotton. *C. R.* 125. p. 865.

due to the same cause may however be shown without the aid of any spectroscope whatever. It is well-known that the sodium flame is a very strong absorber of light of the same wave-length. The light of a sodium flame is viewed through a second sodium flame at a somewhat lower temperature. On these conditions the second sodium flame appears as a dull patch on a much brighter background. If a strong magnetic field is now applied to the hotter source of light, the wave-lengths of the light emitted by it will be slightly altered, and the absorption due to the second flame will be found to be very much less marked, for it will appear less dull as compared with its background. This phenomenon is more pronounced when viewed along the lines of magnetic force, for of course when the line of sight is at right angles to the field, the wave-length of the central line is not altered, and hence the change in the amount of absorption which takes place is not the same. There can be no doubt that in the atoms of the elements there are negatively charged electrons, the motion of which produces the effects we have noted, and that the mass of these electrons is the same for all the elements, and is less than $\frac{1}{1000}$ that of the hydrogen atom; but the nature of the surroundings in which this rapid motion is taking place remains yet to be discovered.

Some years ago Mayer carried out a series of experiments which clearly show the positions which a number of like magnetic poles, if free to move, will take up, when placed in the field of a much stronger pole of opposite

kind. To do this he suspended a powerful bar-magnet with its positive pole downwards. On the surface of some water placed beneath this magnet, corks were floated in which small magnets were stuck so that in all cases their negative poles projected. By this means he proved that when no more than five small magnets were present, they could arrange themselves in a ring owing to the attraction due to the large magnet, and their mutual repulsions. If six were present the arrangement was a ring of five with one at the centre. No more than two rings were formed until the number of small magnets exceeded fourteen, and so on.

In 1904 Professor J. J. Thomson [1] worked out this idea in a mathematical manner with respect to the possible arrangement of the electrons in the atom. His calculations are based on the assumption that the remainder of the atom consists of a uniform sphere of positive electrification, the detailed structure of which he does not specify, and that the negatively charged electrons are revolving in this sphere under the influence of the attraction due to the positive charge, and their mutual repulsions.

By the assumption of such an internal arrangement of the electrons it is quite easy to build up a series of elements which should exhibit periodicity in their properties, if we allow the number of electrons and their arrangement to bestow upon the elements their characteristic properties. Thus when 64 is the total number

[1] *Phil. Mag.*, March 1904.

of electrons present the arrangement in rings is 4, 10, 13, 17, 20 ; while for a total of 44 it is 4, 10, 13, 17, and for 27 it becomes 4, 10, 13. In all these cases the structure, so far as the number of electrons in the internal rings is concerned, is precisely the same.

The following table illustrates one series of the arrangements so worked out.

Total Number of Electrons present.	59	60	61	62	63	64	65	66	67
Numbers in the successive rings.	2	3	3	3	3	4	4	5	5
	8	8	9	9	10	10	10	10	10
	13	13	13	13	13	13	14	14	15
	16	16	16	17	17	17	17	17	17
	20	20	20	20	20	20	20	20	20

It can be easily understood, that if the total number of electrons present is increased, so that it becomes necessary for a new outer ring to form in order that equilibrium may be maintained, in the first case in which the new outer ring appears, that ring will have very little stability ; this for example would be the case when the total number of electrons was 59. No electron however would be likely to be given off, since this would necessitate an entirely new internal arrangement in which the number of rings would be one less. Such an arrangement may therefore be looked upon as similar to that in those elements which exhibit no valency.

When sixty electrons are present the stability of the outer ring is greater, but a negative electron could be very easily emitted, leaving a positively charged body behind. This would thus represent an arrangement which might be expected in electro-positive, monovalent elements such as those of the alkaline group. As the total number of electrons increases from 60 to 67, the stability increases, and the ease with which negative electrons can be emitted diminishes, hence the electro-positive nature also diminishes.

Thus when 61 are present, it is possible for 2 electrons to be emitted, but they can only escape with greater difficulty than a single one can in the case of 60 electrons, so such an element would be divalent but less electro-positive than when 60 are present. When 62 are present, the element would be trivalent, and still less electro-positive. For 63, it would be just as easy for the element to gain four electrons as to lose four; so that it may be looked upon as tetravalent but electrically neutral; then with 64, 65, and 66, the tendency to gain 3, 2, and 1 respectively, will be much greater than the tendency to lose 5, 6, and 7 respectively, so these will represent electro-negative elements, 64 being trivalent, 65 divalent, and 66 monovalent. Should one be added to 67, an absolutely new arrangement of rings must take place, besides, this is the most stable of all the series given, so that it is not at all likely to lose an electron. Here again then we meet with no valency.

To account for the periodicity in properties displayed

by the chemical elements by referring them to such arrangements as that given above would necessitate that each element should contain a large number of electrons.

We have no certain knowledge of the total number of electrons contained in the atom of any element. The only electrons with which we become acquainted are those which break free from their atomic environment, and these may only represent a very small fraction of the total number present.

Sir J. J. Thomson [1] has brought forward arguments to prove that the number of electrons contained in any atom is of the same order as the atomic weight of the element concerned. If such should be the case it would be extremely difficult to explain some of the effects observed. Thus the number of lines in the spectrum of iron which exhibit the Zeeman Effect is greater than the number which expresses its atomic weight when referred to hydrogen as unity. This of course presupposes that such lines are all due to the vibrations of electrons in the metal, but this is by no means certain.

On the other hand, N. Campbell,[1] assuming that in the case of radio-active substances the energy of explosion is derived from rotating electrons falling towards the centre of rotation, has calculated that the number of electrons in the radium atom must be greater than 1200.

For the present however this must remain an open question, which, if solved, might lead towards the solu-

[1] *Phil. Mag.*, June 1906.
[1] *Camb. Phil. Soc. Proc.*, 14, pp. 287 *et seq.*, 1907.

tion of the problem as to the nature of the remainder of the atom.

As previously stated, Sir J. J. Thomson looks upon that remainder as consisting of a homogeneous sphere of positive electrification in which the negative electrons revolve in their orbits, the total positive charge being equal to the sum of the negative charges when the system is in equilibrium. But another possibility suggests itself. Might there not exist positive electrons of a mass whose magnitude is of the same order as that of the negative electrons, and the arrangement of which is such that they are able to perform the same functions as a homogeneous positively electrified sphere ?

Some physicists are of opinion that they already possess experimental evidence of the existence of such positive electrons. M. Jean Becquerel [1] has found when examining the spark spectrum of yttrium that one group of the lines exhibit the ordinary Zeeman Effect when the source of light is subject to the action of a magnetic field, but another group give an inverse effect, that is to say the electrons whose orbits are performed in a clockwise direction have their motion retarded instead of accelerated, and *vice versâ*. This phenomenon he attributes to the presence of positive electrons. The same author writing to the *Philosophical Magazine*, July 1908, uses this line of argument to explain some complex results obtained when examining the band $\lambda 5770$ of the spectrum of the mineral tysonite.

[1] *C. R.* 146, March 1908.

He [1] also imagines that he has been able to separate these positive electrons for a very brief moment when using a discharge through a vacuum tube. The arrangement however that was used by him on this occasion, was such as to render it doubtful whether he actually succeeded in doing this.

R. W. Wood [2] and Dufour [3] have also contributed evidence of a similar nature, but until some further evidence which does not depend entirely on the Zeeman Effect is brought forward, we cannot be absolutely sure that there are positive electrons which are the counterpart of the negative electrons.

Up to the present the great bulk of experimental evidence goes to show that the smallest free positively charged body, known as the positive ion, has a mass of the same order as that of the hydrogen atom.

In 1886 Goldstein, when working on the discharge through a vacuum tube, made use of a perforated cathode, and was able to distinguish faint luminous streaks passing through the perforations into the space behind the cathode with respect to the anode. These rays produced a phosphorescent effect on the glass, which was in all cases quite different from the green phosphorescence produced by the cathode rays.

Many years later (1898) Wien was able to show that these rays, which Goldstein had called "Kanalstrahlen," could be deflected by means of a powerful magnetic field,

[1] *C. R.* 147 (2). [1] *Phil. Mag.* (15), pp. 274-279, 1908.
[3] *C. R.* 146, pp. 118-20.

and the direction in which they were deflected was such as would have happened if they carried a positive charge. In 1907 Professor J. J. Thomson [1] examined the ratio of the charge to the mass for these carriers of positive electricity, and for this purpose he used the discharge produced through highly exhausted tubes. The gas in the tubes was varied, hydrogen, air, CO_2, neon, and helium being tried, but in every case he found that the values of the ratio $\frac{e}{m}$ for the positive ion were such as would result if the charge 'e' was equivalent to that carried by the negative electron, while 'm' was equivalent to the mass of an atom of hydrogen, or in some cases to the mass of an atom of helium.

Rutherford [2] has recently come to the conclusion that the positively charged α particles emitted by radio-active substances are in reality helium atoms.

This is a most important step, since helium must thus be looked upon as a common constituent of all the radio-active substances. In the light of this we can also affirm that the transformations which take place in the uranium series are brought about by the expulsion of α particles.

Many other changes in the atom are known to take place, during some of which negative electrons are emitted; but although these changes may produce some minor

[1] *Nature*, Nov. 12, 1908.

[2] *Proc. Roy. Soc.*, Aug. 1908. See also *Phil. Mag.*, 17, pp. 281-286, Feb. 1909.

internal rearrangements in the atom, no appreciable alteration takes place in the atomic weight, and the element is still considered of the same nature. A time however arrives when the sum of all these minor changes has become so important that an altogether different arrangement becomes necessary. Then it is that one or more α particles are expelled and birth is given to a new element.

Rutherford [1] gives the following list of derivatives from uranium, on the assumption that the changes take place when an α particle is emitted, and that the mass of an α particle is the same as that of the helium atom.

The atomic weight of uranium being taken as 238·5, we have uranium X=238·5−2α particles, that is 230·5, also ionium=230·5, then ionium−α particle=radium =226·5, radium A=222·5, radium B=218·5, radium C=214·5, radium D, radium E, radium F (radio lead) =210·5; also polonium=206·5, and the final product of radium after the transformation of polonium=206·5, a quantity which is almost exactly the recognized atomic weight (206·9) of lead, which substance has been looked upon for some time as likely to represent the final stable product of the series of transformations above described.

Rutherford [2] has now designed a method by which it is possible to actually count the number of α particles emitted by radium, and Sir J. Dewar [3] has been able

[1] *Nature*, Nov. 5, 1908.
[2] *Proc. Roy. Soc.*, Aug. 1908.
[3] *Proc. Roy. Soc.* (81), p. 80.

to experimentally determine the volume of the helium given off in a given time by a definite mass of radium. When the results obtained from these two experiments are compared they are found to agree within the limits of experimental error. The transformations brought about by the expulsion of α particles may therefore be taken to represent with some degree of accuracy what actually takes place in the formation of the uranium-radium series. It is very curious too that hydrogen(?) should be so consistently found in the canal rays, even when the greatest care has been exercised in order to free the tube from all traces of that gas. It would in fact seem that other elements may under certain conditions be able to split up into these position ions which have masses equivalent to that of an atom of hydrogen, and negative electrons having very much smaller masses.

M. Jean Becquerel [1] on the other hand tries to explain the very rapid disappearance of the so-called positive electrons which he thinks he has obtained in vacuum tubes, by their recombination with free negative electrons, or negative ions, to form the hydrogen which is always found when a discharge takes place through a Crookes' tube.

Whatever the ultimate structure of the atom may be, it is quite clear that we must no longer regard it as an indivisible whole, and also that the negative electrons with which we have become acquainted are intimately connected with the atomic structure.

[1] *C. R.*, 147 (2), 1908.

Further, the facts related with respect to the presence of hydrogen in vacuum tubes, and the α particles being identical with the helium atom, would encourage us to believe that these two elements may together form the electro-positive sphere in which the negative electrons revolve. It can be quite readily seen that elements having atomic weights as diverse as those of the chemical elements, could be built up with a suitable admixture of protons of atomic weights 1 and 4 respectively, and if a sufficient number of electrons are also present, the divergence of the atomic weights from whole numbers, can likewise be accounted for, since it must be remembered that only 100-200 would be required to make a difference of ·1 in the atomic weight.

Again, the spectroscopic analysis of the light of nebulæ, which are the simplest and probably the first formed of all the heavenly bodies, reveals the presence of hydrogen and helium only, of all the chemical elements, while many other elements are known to be present in the stars. Hence, if these represent two stages in the evolution of the heavenly bodies, hydrogen and helium may be looked upon as the protons of the other elements. The transformation processes are going on in radium, and the other radio-active substances at a sufficiently rapid rate, as to be capable of being detected, and Sir W. Ramsay among others has hoped to be able to show the transmutation of some of the other elements. He has gone so far, in fact, as to state that he has actually been able to degrade copper to form lithium. Mme.

Curie and Mlle. Gleditsch [1] have repeated these experiments, but have failed to confirm the formation of lithium. Yet, although it may never be possible to transmute one element into another, it does not follow that analogous elements do not represent different stages of development, nor does it even follow that the ultimate structure of the individual atoms are not similar, and it may even be that ultimate particles of all atoms are of precisely the same nature.

[1] *C. R.* 147 (6).

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